

Characterization of Ethyl Valerate Combustion by Analyzing Low Pressure Flames

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In Memorium

*In memory of my young and beloved sister TSHIBOLA ELA
MEJI BABADI Laureine for the brotherly love that united us and
of Prof.Dr. KABWE WA BIBOMBE Charles for inspiring me.
Let the land of our ancestors where they rest with you from now
on will always be soft and light.*

MBUYI KATSHIATSHIA Haddy

”Musuminyina katu ubula :
the persistent never fails”.
”Tshiadima umwe tshiadia bangi”.

”Luba proverbs”.

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Introduction

The increasing demand for energy, the decreasing availability of fossil fuels, and the climate changes are important challenges of this century. To alleviate these issues, scientists propose to diversify the energy mix including a major contribution from biomass also in the form of biofuels [1, 2, 3].

Biofuels produced from biomass via biochemical processes including hydrolysis, hydrogenation and esterification reactions present similar properties with fossil fuels. These traditional fuels (gasoline and gasoil) are used in many industrial applications such as boilers, furnaces and for transportation. But, they have the disadvantage of producing pollutants.

These biofuels can be in solid, liquid or gas phase. Each of this form of biofuels can be used in replacement of traditional fuels according to its physicochemical properties. Solid fuels such as wood, charcoal and pellets are used in replacement of coal in boilers and furnaces. Biodiesel and bioethanol in liquid phase are used in automotive applications in replacement of gasoil and gasoline, respectively. Finally, gas fuels such as syngas (hydrogen, methane, carbon monoxide) can be used in boilers and for the production of electricity in replacement of natural gas. They are also used to produce ammonia for the fertilizer industry and methanol for the production of biodiesel.

Before using these new fuels, their combustion characteristics have to be determined to control if their combustion mode is clean and safe compared to traditional fuels.

Nowadays, scientists underline the advantages of their utilization due to their neutral carbon cycle. Indeed, the quantity of CO_2 absorbed by a plant via the photosynthesis while growing up is equal to the release quantity of CO_2 produced during its combustion. However, the determination of the CO_2 balance includes more than these considerations. In the case of biofuels combustion, the reactants used for its production, such as acid, alcohol, etc., have been ob-

tained from thermochemical processes that consume energy, and thus involved CO_2 emissions. Obtaining the carbon balance of biofuels is quite complex and requires a complete Life Cycle Analysis approach.

Another challenge is the formation of pollutants such as Polycyclic Aromatic Hydrocarbons (PAH), oxygenated compounds (CH_2O , CH_3CHO) and soot particles [4]. Soot are known as carcinogen products [5]. Aldehydes are also known as toxic compounds and their decrease in combustion emissions is necessary [6, 7].

Several liquid fuels can be produced from biomass and among them valerate esters (methyl, ethyl, propyl, butyl and pentyl) [8]. These esters have similar properties to traditional fuels such as gasoline and gasoil. They can, therefore, be used in automotive applications [9, 10]. The lightest ones such as methyl, ethyl and propyl valerate can be used in replacement of gasoline in spark ignition engines. In compression ignition engines, the heaviest ones such as butyl and pentyl valerates can be employed.

Their energy density, storage, energy balance and transportation as fuels are similar to traditional fuels and confer them an advantage for their utilization. One of these second generation biofuels considered in our study is "Ethyl valerate" also called "Ethyl pentanoate" (*EPE*). This ethanolic ester is produced from biomass via chemical processes such as hydrolysis, hydrogenation and esterification reactions [8]. Its combustion characterization is the best way to know if it has a clean and safe combustion. Currently, there are not many studies in the literature about ethyl valerate's combustion characterization. Dayma et al. [11] studied this ester in a jet stirred reactor and in a spherical combustion chamber in order to characterize its combustion at high pressure (10 atm). Contino et al. [10] investigated its combustion in replacement of gasoline in pure and blended forms in a spark ignition engine.

To characterize in details a fuel combustion, a flame structure study at low pressure is an important step. The low pressure allows to analyze all the intermediate species formed and consumed during combustion and the principal products such as CO_2 , H_2O , CO , and H_2 .

Many hydrocarbons have been investigated at low pressure to characterize their combustion and to elaborate detailed kinetic models describing the different fuel consumption pathways. Oxygenated fuels are now promoted in different applications, specifically, due to the oxygen contents in their chemical structure. The presence of oxygen seems to have an effect on the pollutants reduction.

For this reason, the characterization of this type of fuels is necessary at low pressure to control the aldehydes formation, although these fuels are used at high pressure in real applications.

This study thus focuses on ethyl valerate combustion by analyzing premixed flat flames at low pressure in order to characterize in details its combustion.

To reach our objectives this thesis dissertation is divided into four chapters:

1. The first chapter describes the origin of biofuels and their evolution in time from primary to secondary biofuels. The conversion from biomass to biofuels via different physicochemical processes is also presented in this chapter. Finally, the utilization of these biofuels in combustion at high and low pressure is illustrated.
2. The second chapter shows the development of the experimental setup including the evaporation system, the combustion chamber, the compression system and the analysis technique. In this work, gas chromatography is used to separate, analyze and identify all stable chemical compounds involved in the ethyl valerate combustion. The measurement of the temperature profiles using a thin thermocouple is also discussed in this chapter.
3. In Chapter 3, the *Cosilab*®[12] software is used to simulate, numerically, the ethyl valerate combustion including its detailed consumption pathways using different equations according to the mathematical description of one-dimensional premixed flame.
4. The chapter 4 presents the results and discussion of the work. At different equivalence ratios, the experimental and the simulated mole fraction profiles are compared to check the reliability of the detailed kinetic model and to improve it. The different ethyl valerate consumption pathways are described thanks to the numerical simulation results. The mechanism is tested against the ethyl valerate laminar burning velocities at atmospheric pressure. Then, The kinetic model is tested and validated against the experimental data in a jet-stirred reactor at high pressure.

Finally, this thesis dissertation ends with the general conclusions and perspectives.

Chapter 1

Biofuels and Combustion

Introduction

The pollution reduction linked to the fossil fuel combustion is the main challenge of these decades. Biomass has already been used to produce heat and electricity. To diversify the energy resources, scientists propose a significant contribution of biomass in energy production. The biomass can be used in solid form (pellets), liquid form (biodiesel or bioethanol) and gas form (syngas) to replace traditional fuels such as coal, gasoline and gasoil.

In this chapter, the classification of different biofuels is presented from the primary to the secondary biofuels. The biofuels obtained from biomass using thermochemical and biochemical processes are also described in this study. The secondary biofuels are divided into the first, second and third generation. From all the second generation biofuels, ethanol is the most common in replacement of gasoline [13, 14]. Second generation biodiesel is used in replacement of gasoil [15]. Ethanol and biodiesel can also be produced as first generation biofuels according to the nature of the feedstock used during their synthesis. The synthesis and the utilization of second generation biofuels in combustion are also described for the specific case of ethyl valerate.

1.1 Classification of Biofuels

Biofuels are liquid, solid or gas produced from biomass. According to their origin and phase, these biofuels are classified as primary and secondary biofuels [14].

1.1.1 Primary biofuels

Primary biofuels are natural such as the unprocessed biomass (fuelwood and wood chips) and the processed biomass (pellets). They are in solid form and they can be used without any chemical or biological treatment. They are directly combusted for cooking, heat or electricity production in industrial processes [14].

Primary biofuels can also be transformed to produce Secondary biofuels.

1.1.2 Secondary biofuels

Secondary biofuels are produced by processing biomass and can be in solid form (charcoal), liquid form (ethanol: C_2H_5OH , biodiesel and bio-oil) or gases (biogas: CH_4 and hydrogen: H_2) [14].

In most cases, liquid biofuels can be used directly in engines or blended with fossil fuels for various industrial processes [14].

Different technologies are used to extract energy from biomass and to produce secondary biofuels. These technologies are divided in two main routes: thermochemical and biochemical.

The complete scheme including thermochemical and biochemical processes for the production of the biofuels is presented in Figure 1.1.

1.2 Thermochemical processes

In thermochemical conversion, both thermal and chemical steps are used to convert biomass into biofuels.

In the first thermochemical process, biomass is combusted directly without any transformation to produce heat (Figure 1.1).

Gasification that leads to the transformation of a raw material into a gaseous mixture, is the second thermochemical process as depicted in Figure 1.1. The

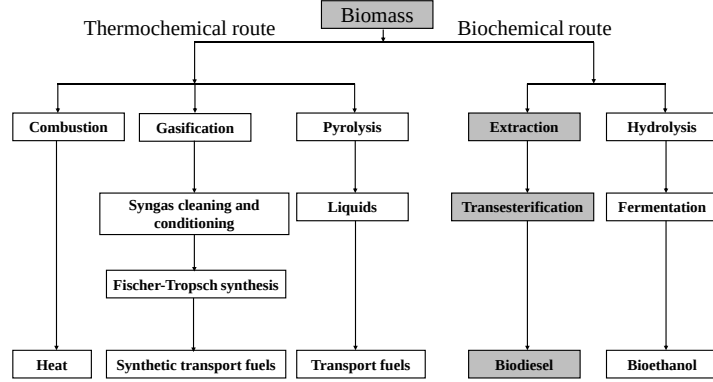


Figure 1.1: Simplified schematic illustration of the two main biofuel production pathways [16].

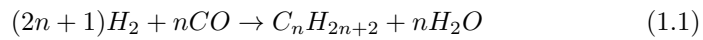
gaseous product is a mixture of H_2 , CO , CO_2 , CH_4 , C_2H_4 and impurities such as nitrogen, sulfur, alkali compounds and tars [16, 17]. The reactions of this process are listed in the following Table 1.1.

Table 1.1: Basic gasification reactions [16].

Reaction	$\Delta H(kJ/mol)$
$2C + O_2 \rightleftharpoons 2CO$	+246.4
$C + O_2 \rightleftharpoons CO_2$	+408.8
$C + CO_2 \rightleftharpoons 2CO$	-172
$C + H_2O \rightleftharpoons CO + H_2$	-131

Fischer-Tropsch's synthesis includes a set of chemical reactions in a mixture of hydrogen and carbon monoxide (syngas) to produce long chain liquid hydrocarbons. This process was developed by Franz Fischer and Hans Tropsch in 1920 and is operated at high pressure (10 atm), at the temperature range of 150-300°C. Its product is a synthetic petroleum that can be used in the automotive application [16].

The Fischer-Tropsch's synthesis is summarized in this chemical reaction (Equation 1.1):



where n represents the length of the hydrocarbon chain.

Pyrolysis is the third thermochemical method. It consists of the biomass degradation without the utilization of oxygen. It produces charcoal (solid), bio-oil (liquid) and gaseous products [18]. Pyrolysis bio oils and gas can be used to produce new generation biofuels [19].

For example, Ngoc Bui et al. [19] studied the hydrodeoxygenation of guaïacol (oxygenated molecule representative of pyrolysis bio oil) with a straight run gas oil in the framework of a hydrosulfurization process. They concluded that hydrocarbon compounds can be synthesized from the guaïacol as depicted in Figure 1.2.

In Figure 1.2, the meanings of the abbreviations are:

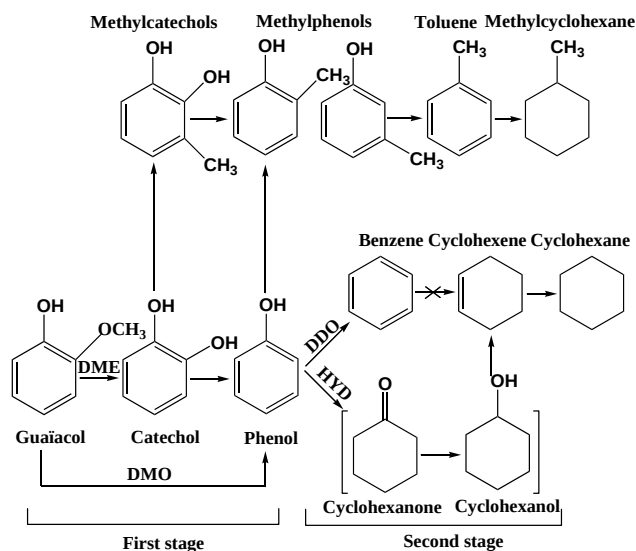


Figure 1.2: Reaction pathways for the conversion of guaïacol at 573 K under 4 Mpa of H_2 on a CoMo on alumina sulfide catalyst [19].

- DME: demethylation,
- DMO: demethoxylation,
- DDO: direct hydrogenolysis of the C-O bond between the aromatic carbon and the OH and
- HYD: preliminary hydrogenation of the aromatic ring before elimination of the OH groups.

The liquefaction, which is also a thermochemical process in the biofuel production, has been investigated in the presence of solution of alkalis, propanol, glycerine and butanol [18]. In this technique, biomass (lignocellulosic materials) can be converted directly into a liquid which is similar to heavy fuel oils by reacting the synthesis gas in the presence of suitable catalysts [18].

Gasification or pyrolysis can be used for the production of biodiesel. However, high temperatures and pressures are required [14].

To reduce the extreme temperature and pressure constraints, biochemical processes can be used.

1.3 Biochemical processes

Biochemical and chemical processes are used to produce liquid biofuels such as ethanol and biodiesel, respectively, from edible and non-edible feedstock (Figure 1.1).

Hydrolysis and fermentation are the main steps in the production of bioethanol from biomass. Extraction (including solvents) and transesterification are used in the production of biodiesel [14, 16, 18].

The liquid biofuels obtained by these techniques are classified into three groups:

- first generation
- second generation
- third generation

The differences between the three groups are the nature of the feedstock used for their production.

1.3.1 First generation biofuels

The first generation fuels are liquids made from starch, sugar and vegetable oil [13]. The label "first generation" is linked to the feedstock used for their production that are competing with food supply and are not sustainable.

This generation requires simple but energy consuming processes such as physical process (pressing), fermentation (yeast), distillation and dehydration to obtain the biofuels. The first generation liquid biofuel most used in industrial applications is ethanol called "Bioethanol". Gomez [13] proposed a bioethanol

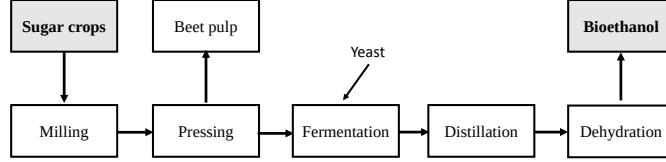


Figure 1.3: Bioethanol production process from sugar crops [13].

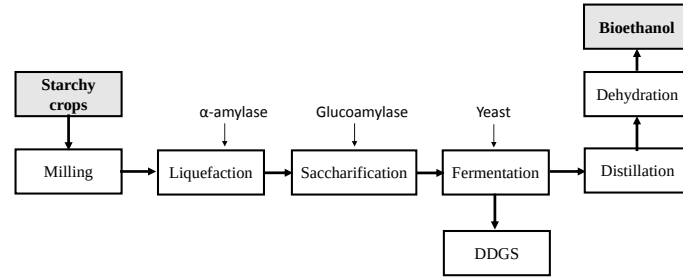


Figure 1.4: Bioethanol production process from starchy crops (DDGS: Dry Distilled Grain with Solubles) [13].

production process from sugar crops and from starchy crops, as shown in Figures 1.3 and 1.4.

Bioethanol can be produced from organic based matter with high contents of sugars, by fermentation using enzymes produced from yeast [14]. The enzymes are used to convert glucose (sugar with six carbon atoms) into ethanol. The fermented matter containing alcohols and others chemical compounds such as water and by-products, is distilled and dehydrated to obtain bioethanol.

The other first generation liquid biofuel is biodiesel that can be used as fuel in diesel engines. To produce first generation biodiesel, vegetable oils are upgraded with physical and chemical processes.

The physical conversion consists in the compression of grains to extract vegetable oil [20]. This process can be performed in dry and hot conditions. To increase the extraction yield, Norris [21] proposed the wet milling. The presence of water in grains allows to have an immiscible phase due to the contact between water and oils. The yield of the wet milling method is 70% against 40% obtained from dry extraction. The obtained oil must be kept in a dry condition to avoid oxidation due to the contact between air and oil. While extracting in hot conditions, oils can be oxidized to produce anhydride acids

then the dry extraction of damp grains seems to be promoted.

Vegetable oils do not have similar physicochemical properties with fossil gasoil fuel. To improve their properties (density, viscosity, etc.), a chemical process is needed. This chemical process is known as "Fischer transesterification" and it uses methanol [13, 14, 22]. Then, the transesterified biofuels can be used as fuels in compression ignition engines [23, 24].

Transesterification is a chemical reaction proposed by Fischer for the conversion of glycerides from oil into esters (biodiesel) and glycerol (by-product), using an alcohol as reactant and a catalyst [25, 26]. The catalyst can be an acid (H_2SO_4) or a base (NaOH or KOH).

Chemically, biodiesel is a fatty acid monoalkylester containing a long chain from vegetable or animal oils (Figure 1.5).

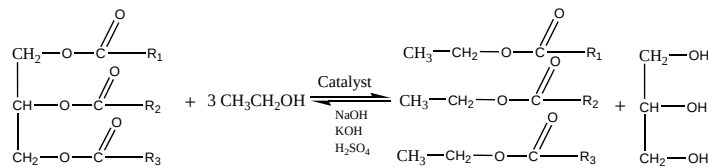


Figure 1.5: Transesterification reaction: reactants (triglycerides + alcohol) and products (esters/biodiesel+glycerol) [26].

Transesterification is a reversible reaction. To produce biodiesel, alcohol is used in excess to the vegetable oil (triglycerides) by a ratio of 3-1 to promote the forward reaction. Otherwise, if the vegetable oil and the alcohol are in the same proportion, at the end of the reaction, both reactants and products will coexist in the reaction medium. After the chemical reaction (transesterification), the products and the catalyst are separated physically (decantation) to obtain the biodiesel. The biodiesel produced in this way has similar physicochemical properties with gasoil [27].

Methanol is used as the alcohol in the transesterification and the obtained esters are called "methyl esters".

The first generation liquid biofuel has the major inconvenient of being in conflict with food supply. For this reason, scientists proposed to diversify the production of liquid biofuels by using none-edible biomass.

1.3.2 Second generation biofuels

Second generation biofuels are deemed "greener" because they do not compete with food supply. They are made from sustainable feedstock. The term sustainable is defined by the availability of the feedstock.

The chemical processes described before are used in the production of this generation of liquid fuels (extraction + transesterification). In order to use them like first generation biofuels, the second generation fuels has the particularity of being converted before their utilization.

Pure vegetable oils are considered also as fuels in general. If they are obtained from non-edible biomass such as jatropha, they are deemed "second generation" biofuels. Otherwise, if they are obtained from edible biomass such as palm, sunflower, etc. they are classified as "first generation" biofuels.

1.3.3 Third generation biofuels

The biofuels produced from algae are considered as the third generation biofuel. Algae has an advantage of producing highly unsaturated oils. The unsaturated oils are more volatile, particularly at high temperatures. Due to these properties, they can be used in automotive applications. The disadvantage of these unsaturated oils is the fact that they are easily oxidized and thus more prone to degradation. The advantages of biodiesel produced from algae are: high growth rate, high lipid yield, high environmental tolerance, low competition for arable land and potable water and finally non seasonal limitations in production [28, 29, 30]. Microalgae biomass production will effectively improve the biofixation of waste CO_2 (1 *kg* of dry algae biomass utilize about 1.83 *kg* of CO_2) [31].

This generation of biofuels is still now in the development phase.

1.4 Valeric ester synthesis

In this section, we present the synthesis of esters (second generation liquid biofuel) from biomass. The main route used in this section, is the biochemical process which allows to synthesize biofuel through the following steps:

- hydrolysis
- hydrogenation

Table 1.2: Reaction steps and key performance factors for individual process steps: reaction selectivity ([mol%]), productivity ($[t_{\text{product}}m_{\text{reactor}}^{-3}h^{-1}]$) and concentration ([wt%]); IER: acidic ion exchange resin [8].

	1	2	3	4
	Hydrolysis	Hydrogenation	Hydrogenation	Esterification
Catalyst	H ₂ SO ₄	Pt/TiO ₂	Pt/ZSM-5	IER
Selectivity	50 – 60	> 95	> 90	> 95
Productivity	> 0.1	> 10	> 1	> 0.02
Concentration	< 5	> 90	> 50	> 50

- esterification

In this work, we focus on esters produced from biomass, called "valerate esters". Valerate esters are biofuel containing a pentanoate radical (C₅). Lange et al. [8] proposed a synthesis of such esters from biomass (Figure 1.6 and Table 1.2). This chemical treatment includes hydrolysis, hydrogenation and esterification. If ethanol is used during esterification reaction, the obtained valerate is called "Ethyl valerate or ethyl pentanoate". If methanol is used, the obtained ester is "Methyl valerate or methyl pentanoate".

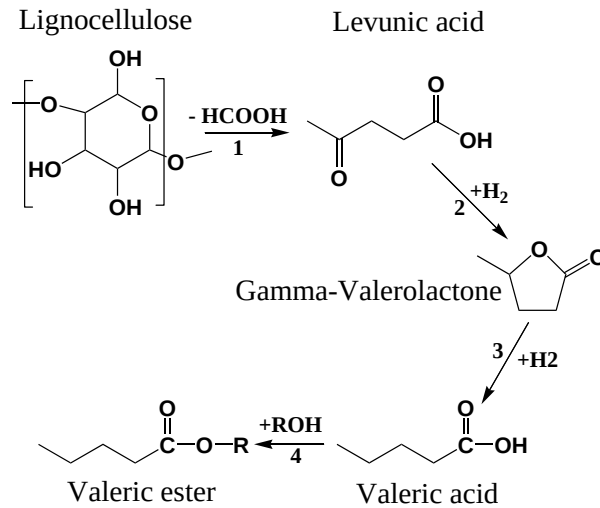


Figure 1.6: Reaction scheme: from biomass to valerate ester [8].

To produce valeric biofuels from lignocellulosic materials (Figure 1.6), the acid hydrolysis is used to convert lignocellulosic into levunic acid. The hydro-

genation of the levunic acid produces γ -valerolactone. This chemical compound is converted into valeric acid by hydrogenation. Finally, esterification reaction, in the presence of ethanol, produces ethyl valerate [8].

Valeric acid which is a stable chemical compound produced before valerate esters cannot be used in automotive applications due to its acid properties that can damage the engine.

Levunic acid is one of the important intermediate chemical compounds in the production of valeric biofuels from biomass [32]. γ -valerolactone that is produced from levunic acid is the second important stable chemical compound in order of appearance in the valeric esters production [33].

Another transformation way from lignocellulosic to levunic acid, is also proposed by Raspolli Galletti [34] (Figure 1.7).

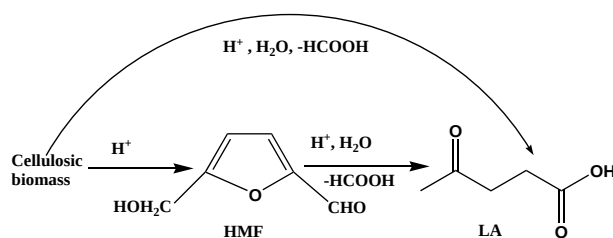


Figure 1.7: Reaction scheme: from lignocellulosic material to levulinic acid [34].

In this process, the 5-hydroxymethyl-2-furaldehyde (HMF) is a product of the acid-catalyzed dehydration of cellulosic biomass at mild temperature. This molecule can be used in the synthesis of several pharmaceuticals and fine chemicals. Furan-based polymers are also used as a biobased replacement in plastic [34]. To obtain levulinic acid from this molecule (HMF), a subsequent rehydration (acid hydration) follows by the abstraction of formic acid is used. The levulinic acid (LA) can be used in the synthesis of valeric acid then valeric esters. Other important molecules use in automotive applications such as fuel additives and liquid hydrocarbon fuels can also be produced from biomass. The synthesis of these molecules is proposed by Climent et al. [35].

The valerate esters produced from biomass are methyl valerate, ethyl valerate, propyl valerate, butyl valerate and pentyl valerate. The difference between these valerates is due to the alcohol used during the esterification reaction:

methanol, ethanol, propanol, butanol or pentanol, respectively. Their chemical structures are presented in Figure 1.8.

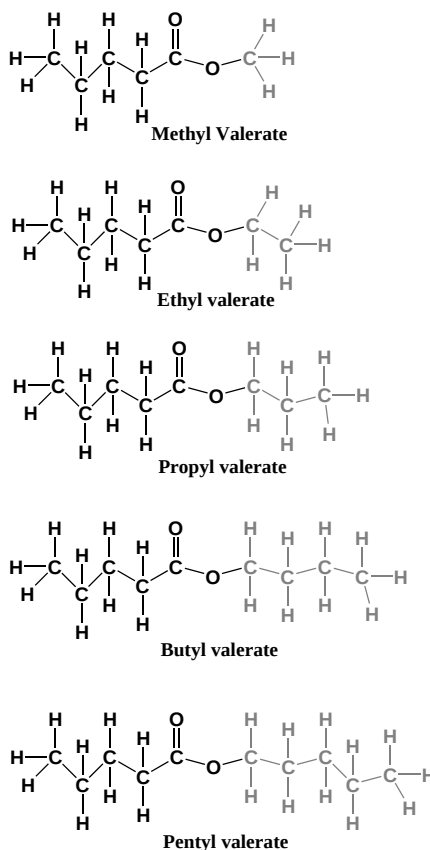


Figure 1.8: Chemical structures of methyl, ethyl, propyl, butyl and pentyl valerates.

Table 1.3 presents the valerate properties compared to gasoline and gasoil.

The blending research octane number (BRON) is used, in comparison to gasoline, for the utilization of fuels in spark ignition engine. For the diesel engine, the derived cetane number (DCN) is used as the reference parameter.

Based on the physicochemical properties of the different valeric esters as depicted in Table 1.3, methyl, ethyl and propyl valerate can be used in replacement of gasoline in spark ignition engine. Then, butyl and pentyl valerate can be used in a compression ignition engine due to the values of their DCN that are similar to the reference gasoil.

Table 1.3: Main properties of valerates compared to gasoline and gasoil [9, 10]. n.a. : non available.

	Density	LHV	A/F_{st}	T_{boil}	$LHV/(A/F)_{\rho N}$	T_{flash}	BRON	DCN
	$15^{\circ}C [kg/l]$	$[MJ/kg]$		$^{\circ}C$	$[MJ/m^3_{cyl}]$	$^{\circ}C$		
Methyl	0.875	28.8	9.5	137	3.91	22	~ 115	n.a.
Ethyl	0.874	30.3	10.1	142	3.88	34	~ 100	17 ± 1
Propyl	0.870	31.5	10.6	167	3.86	38	~ 90	n.a.
Butyl	0.868	32.6	10.9	187	3.86	67	n.a.	24.5 ± 1
Pentyl	0.874	33.5	11.2	206	3.85	76.5	~ 10	30 ± 1
Gasoline	0.691	44.66	15.1	99	3.82	-8	95	n.a.
Gasoil	0.835	42.91	14.6	245-345	3.81	55	n.a.	53 ± 1

1.5 Esters in internal combustion engines

Combustion is a complex process including fuel and oxidizer. The complexity of the combustion is due to the number of species (radical and stable) formed and consumed, and the heat released during this phenomena. Species produced and consumed during the combustion depend on the chemical structure of the main fuel, the heat released (energy) and the pressure. Different environments such as burners, reactors and engines, are used to study the aspects of combustion. To reveal chemical details, it is useful to avoid the complex flow fields of turbulent combustion [36].

The compression ignition engine made by Rudolph Diesel, at the end of the 19th century, was running with peanut oil [36, 37]. The utilization of this vegetable oil presents some technical problems such as coking, low viscosity and poor ignition [36]. To alleviate these problems, scientists modified the Diesel engine to adapt it to the fossil gasoil fuel [38, 39].

Nevertheless, the pollutant formation (such as NOx and soot) and the non-neutral carbon cycle of the fuel remain currently the disadvantages in addition with the CO₂ emissions for engines.

The advent of esters produced from vegetable sustainable materials called "biodiesel" is a potential way to solve fossil fuel combustion problems [40]. Biofuels (esters) can be used or blended to fossil fuels. Methyl or ethyl esters, are commonly referred to as "biofuel" because they are synthesized from vegetable oil via transesterification reaction. This name "biofuel" referred to their

utilization as fuels in replacement of gasoil/gasoline or blended to these fossil fuels [37].

In this section, the comparison between valeric esters with the respective fossil fuels is presented in order to assess globally the combustion behaviour of these fuels. To reach this objective, we present the comparison of the emissions between on the one hand gasoil and butyl and pentyl valerate, and gasoline and methyl and ethyl valerate on the other hand.

The high nitrogen oxides (NO_X) and particulate matter (PM) emissions are the main problems with the air pollution using diesel fuel in transportation sector [41].

Esters (biofuels) have similar properties with the traditional fuels, as described before. These biofuels are more attractive for their low sulfur content which allows the use of a catalyst to remove NO_X from lean-burn engine exhaust. These esters are also renewable materials and their oxygen content (10% in average) confer them a property of none soot precursor fuels [42]. Many studies related that these biofuels show an effect on the reduction of pollutants in comparison with the traditional fuels [43, 44].

The butyl and pentyl valerates physicochemical properties compared to gasoil are similar (Table 1.3). According to these properties, Contino et al. [9] characterized their combustion in a compression ignition engine.

The derived cetane number (DCN) presented in Table 1.3 were obtained following the ASTM D7668 standard with a Herzog Cetane ID510 [9]. The cetane number (CN) that is an inverse function of the fuel ignition delay, is an indicator of the auto inflammation properties. This property is used to determine the quality of the fuel in a compression ignition engine. Fuels with high cetane number values have shorter ignition delay than those with lower cetane number. Comparing the values presented in Table 1.3, gasoil has a shorter ignition delay period than pentyl valerate and butyl valerate. The valeric esters present high values of density but are in the average values according to EN-14214 standards that fix this value between 0.86 - 0.90 g/cm^3 [45].

According to the previous specifications, Contino et al. [9] used pure gasoil and blends of 20% in volume of butyl and pentyl valerate to characterize their combustion.

Based on their results, they confirmed that the esters have a lower cetane number and therefore a longer ignition delay. But, the addition of 20% in volume of butyl and pentyl valerate does not affect significantly the performance (IMEP: indicated mean effective pressure) and the emissions (CO_2 , CO, HC and NO_x). Thus, butyl and pentyl valerate can be used as fuels in a compression ignition engine in blends with gasoil.

Contino et al. [10] also studied the engine performance and emissions of second-generation biofuels in spark ignition engines: the case of methyl and ethyl valerate. Methyl and ethyl valerate have similar physical and chemical properties to gasoline as related in Table 1.3.

The blending research octane number (BRON) is a RON number obtained by testing a mixture instead of the pure component. Parameters such as density, viscosity, flash point, ... are also determined to improve the percentage of the biofuels that must be taken into account while blending the studied fuels.

The flash point corresponds to a minimum value of temperature at which a fuel produces a sufficient quantity of vapour in the air to produce a flammable gas mixture in contact with a calorific energy source. The auto-ignition temperature is reached when the gas mixture does not necessitate a calorific energy source for ignition. Usually, the flash point is determined for gasoline (spark ignition engine) and the auto-ignition temperature for gasoil (compression ignition engine).

As for the spark ignition engine, the authors used pure valeric esters and blends of 20% of esters with a reference fuel called "PRF95" (Primary Reference Fuel that is a mixture of 95% volume iso-octane with 5% volume n-heptane) [10]. The thermal efficiencies of the engine with the studied fuels are very closed, compared to the reference fuel.

The authors related that the decreasing of CO_2 emissions are similar for the different fuel mixtures. The observed difference is due to the mass of carbon per kWh of fuel burned. They noticed that its value is 67.7, 77.6 and 76.8 g/kWh for PRF95, methyl valerate and ethyl valerate, respectively. The NO_x emissions have slightly decreased when using valerates. The hydrocarbon emissions of the reference fuel are slightly smaller at high loads and slightly higher at low loads. This is due to the values of CO emissions as reported by

the authors.

There is a slight difference between the reference fuel and the valeric esters due to their physicochemical properties. The authors proposed that the relatively high absolute value for CO emissions is due to the experimental settings. The auto-ignition was also determined by the authors for the reference fuel in comparison with the methyl and ethyl valerates. The results carried out by the authors, show that the esters have a significantly longer ignition delay compared to the reference fuel. The results were determined for an equivalence ratio of 1, at 40 *bar*. The methyl and ethyl valerate present a higher BRON (Blends Research Octane Number) than gasoline as depicted in Table 1.3. This parameter determines fuel's "anti-knock" quality or its resistance to pre-ignition (resistance to detonation). For this reason, Contino et al. [10] proposed to test them in the future in a real application engines and performing their endurance in the same experimental condition.

The authors concluded that the esters propagate faster than the reference fuel which requires a slight change of the ignition timing to optimise the work output. The performances and the emissions are not significantly changed comparing both esters (methyl and ethyl valerates) to the reference fuel (PRF95) [10].

1.6 Experimental setups for biofuel combustion

To predict the biofuel decomposition during its combustion, the chemical structure of the fuel is very important. The detailed kinetic mechanism of biofuel combustion is necessary to predict the formation of pollutants, the heat released and its ignition properties (autoignition delay). Several hydrocarbons have been studied during these last decades, and their combustion modes are well-known thanks to the elaboration of their detailed kinetic models. Oxygenated fuels such as esters, are still not known enough. We note that ethanol and butanol are the most studied biofuels [46].

In this section, we propose some esters applications in combustion by presenting their studies in premixed and non-premixed flames.

The characterization of fuels in combustion can be performed experimentally by using different modes of combustion, combining different apparatuses [47].

These experimental setups used in laboratories are:

- Reactors
- Compression systems
- Burners

1.6.1 Reactors

A reactor is an experimental setup at constant volume in-which a mixture of fuel and oxidizer is burned.

Close reactor

In these reactors, fuels are studied at different steady-state conditions of temperature and pressure. Due to the experimental conditions (long time to reach homogeneous phase), the rapid combustion phenomena cannot be studied in this reactor. Therefore, this technique is useful for slow phenomenon at low temperature.

Tubular flow reactor

In this reactor, the constant pressure is used in diluted medium. This apparatus allows to control the gas temperature and to measure its residence time. Depending on the equivalence ratio and the mixture temperature, the intermediate species and the final products can be analyzed. This reactor also deemed "laminar flow reactor" is used to study an isolated reaction or a multi step reaction mechanism. It can cover a wide range of conditions, such as: temperature (550 - 1200 K), pressure (0.3 - 20 atm) and equivalence ratio (pure pyrolysis to oxygen-rich conditions) [48].

Well stirred reactor

This reactor is also deemed: "perfectly stirred reactor". In this reactor, the volume, the temperature and the pressure are maintained constant and the homogeneity between the chemical compound concentrations is observed, leading to an instantaneously mixture between the fuel and the oxidizer.

Two types are commonly used:

- Longwell’s reactor : it is a spherical reactor with small holes from which the jet of the gases reaches the combustion chamber. In this reactor, the configuration does not allow a perfect mixture. Due to this configuration, the temperature and the chemical compounds concentration are not homogeneous.
- David and Matras’s reactor : in this reactor, the gaseous jets are introducing in order to reach homogeneous condition between the different chemical compounds in the combustion process. This reactor is also deemed ”Jet-Stirred Reactor”(JSR) [11, 47].

1.6.2 Compression systems

The characterization of the fuel combustion can also be done using compression systems such as rapid compression machine (RCM) and shock tube.

Rapid compression machine (RCM)

This apparatus allows to compress in some milliseconds a gas mixture of fuel and oxidizer to reach a high pressure and a high temperature, above the autoignition value. Thus, the RCM allows to investigate the autoignition characteristics such as the ignition delay time, the heat release rate, etc. [49]. It can be used for chemical kinetics studies at elevated pressures and temperatures [50].

Shock tube

The shock tube is a close reactor used in the study of chemical kinetics at high temperature and high pressure. This apparatus is also used as the rapid compression machine, to study the chemical reactions at high temperature. Due to its properties, the shock tube also allows to determine the autoignition delay of a fuel gas mixture [51].

1.6.3 Burners

Burners have different configurations depending on the flow arrangement of fuel and oxidizer. They can be designed for premixed mixtures or for diffusion flames.

Premixed flame burner

The fuel is premixed with the oxidizer before the combustion chamber as in a spark ignition engine, etc.

Two sorts of flames are produced from premixed mixture mode:

- Laminar flame: the flame is stabilized at the burner surface and has three parts (fresh gas, flame front and burned gas part). At low pressure, the flame is flat and one dimensional due to the fact that the propagation velocity of the flame is equal to the fresh flow gas. The position reached by the flame in this mode, corresponds to the position at which the two velocities become equals. This type of flames is simple to study due to the fact that it represents only the concentration and temperature gradients in one dimension, perpendicular to the burner surface. The burner used in our study belongs to this type of burners.
- Turbulent flame: the turbulent flame is obtained by adding a grid above the flame. The presence of the grid creates a complex flame front in-which the consumption of the fuel is increased. Due to the increase of the fuel consumption, the heat release is higher than in the laminar mode.

Diffusion flame burner

The combustion between the fuel and the oxidizer can be controlled by the diffusion of both reactants as in a compression ignition engine, a candle, etc. If the mixture is not rapid to reach homogeneous phase compared to the reaction velocity, the obtained flame is diffused. This characteristic is quickly reached when the reactants arrive in opposition. The fuel is then diffused in the oxidizer, and the flame front is created at the two limited flows.

1.7 Methyl and ethyl esters in flames

To study properly the combustion of a specific fuel, different studies at low and high pressure are performed. These studies allow to elaborate detailed kinetic mechanisms for each fuel in order to understand its combustion. These kinetic models allow to predict the formation and the consumption of all species (conversion of reactants, formation of pollutants, formation of soot, effects of additive, ...) for different temperatures, pressures and equivalence ratios.

In this section, we present a short review of the biofuel flame studies. One of

the important class of biofuels commonly used, consists of methyl and ethyl esters (more than 16 carbon atoms in their chemical structure) derived from vegetable and animal oils [1].

Firstly, the study of these esters combustion is presented. Secondly, the small alkyl esters (from C_2 to C_4) combustion in premixed flames will be presented and finally, for those from C_5 to C_{10} will also be discussed. Ethyl valerate is a C_7 alkyl esters and the presentation of esters combustion having less and more than 7 carbon atoms is important to demonstrate the impact of alkyl radical length in ester combustion. The review on these different esters allows to isolate the role of the ester functionality on combustion processes.

In 2011, a detailed kinetic mechanism was developed by Westbrook et al. [52] for five major esters (more than 16 carbon atoms) from soy and rapeseed biodiesel fuels using their oxidation experimental data in a jet stirred reactor and intermediate shock tube ignition. Methyl palmitate ($C_{17}H_{34}O_2$) methyl stearate ($C_{19}H_{38}O_2$) are saturated alkyl chains; and methyl linolenate ($C_{19}H_{32}O_2$), methyl linoleate ($C_{19}H_{34}O_2$) and methyl oleate ($C_{19}H_{36}O_2$) are unsaturated alkyl esters. The authors concluded that the low temperature reactivity, the ignition delay, the autoignition and the cetane numbers are all intimately connected. The saturated methyl esters such as methyl palmitate and methyl stearate have a high cetane number of 86 for the first, and 101 for the second one. Due to their low temperature reactivity and heat release, they present shorter ignition delays. The other methyl esters with low cetane numbers such as methyl oleate (59), methyl linoleate (38) and methyl linolenate (23) and with higher temperature reactivity, present longer ignition delays. The methyl stearate and methyl oleate were also investigated in a jet stirred reactor by Naik et al. [53]. The authors demonstrated that methyl oleate was found to be slightly less reactive than methyl stearate. This is due to the presence of double bonds in unsaturated esters that inhibit certain low temperature chain branching reaction pathways. A detailed kinetic model mechanism was elaborated and validated against experimental data. It contains 3,500 chemical species and more than 17,000 elementary chemical reactions.

Previously, In 2009, Westbrook et al. [54] studied four small alkyl esters rich premixed laminar flames at low pressure. The main objective of the study was to elaborate a detailed kinetic mechanism in order to extend it to larger

oxygenated fuels and then for esters. The four small esters studied are: methyl formate ($C_2H_4O_2$), methyl acetate ($C_3H_6O_2$), ethyl formate ($C_3H_6O_2$) and ethyl acetate ($C_4H_8O_2$). A molecular-beam mass spectrometer, employing tunable vacuum-ultraviolet synchrotron radiation for photoionization was used to study these premixed flat flames at 30 *torr*. The ethyl acetate and the ethyl formate flames produce much higher levels of C_2 species (ethylene is produced directly from the ethyl groups) while the methyl acetate and the methyl formate produce these C_2 species by recombination of methyl groups followed by dehydrogenation. Methyl is found to be a major intermediate species in the four flames. The simulated acetaldehyde mole fraction profile is in a good agreement with the experimental one but its formation pathway is not the same for the two ethyl esters.

The smallest ester (methyl formate) has been also studied in a burner stabilized laminar flames at low pressure (22 - 30 *Torr*) with a range of equivalence from 1.0 to 1.8 for flame conditions of 25-35% fuel by Dooley et al. [55]. The authors used the same analysis equipment as described before in the study of Westbrook et al. [54]. In this study, they related that methanol (CH_3OH) and formaldehyde (CH_2O) are the most prominent intermediate species formed in the high temperature flame oxidation. The detailed kinetic mechanism validated against these experimental data could then be extended to large esters. The radical-radical recombination reactions are shown to be significant in the formation of intermediate species such as ethylene, acetylene and acetaldehyde. It is very necessary to underline the importance of these reactions at high temperature and low pressure.

In 2007, the comparison of saturated and unsaturated C_4 fatty acid methyl esters in an opposed flow diffusion flame and in a jet-stirred reactor was studied by Sarathy et al., at atmospheric pressure [56]. The burner used for the diffusion flame consisted of two opposing identical stainless steel inlets that directed the fuel stream and oxidizer stream into a stagnation point flow. Fuel and oxidizer streams had inlet velocities of 13 and 14 *cm/s*, respectively. The oxidizer stream contained 42% of O_2 and 58% of N_2 for the top burner port; 4.7% of fuel (methyl butanoate : $C_5H_{10}O_2$ or methyl crotonate : $C_5H_8O_2$) and 95.3% N_2 were sent through the bottom. For the jet-stirred reactor, the constant residence time was 0.07 *s*. A high degree of dilution was used to reduce the temperature gradients and heat release in the jet-stirred reactor.

The gas chromatography was used as the analysis technique and allowed to analyse fuels, intermediate species and products of the methyl butanoate and methyl crotonate combustions. For both experiments, the authors concluded that the methyl crotonate combustion produced much higher levels of C_2H_2 , $1-C_3H_4$, $1-C_4H_8$ and $1,3-C_4H_6$ than methyl butanoate. These species can be considered as soot precursors. Moreover, in the opposed flow diffusion flames, methyl crotonate produced benzene but in the methyl butanoate flame, it was not detected.

In 2008, Gail et al. [57] studied methyl esters oxidation in a jet-stirred reactor at atmospheric pressure over the temperature range of 850-1400 K . Methyl(E)-2-butenate ($C_5H_{10}O_2$) and methyl butanoate ($C_5H_{10}O_2$) in dilute conditions with equivalence ratios of 0.375 and 0.75, were also studied under counterflow diffusion flames. They used gas chromatography as analysis technique. For the laminar counterflow flame, the fuel and the oxidizer had inlet velocities of 13 and 14 cm/s , respectively. The GC system measured $C_1 - C_5$ alkanes, alkenes, alkynes and benzene. The fuels (methyl(E)-2-butenate and methyl butanoate) and O_2 , the intermediate species (formaldehyde, methanol, acetaldehyde, acetylene, propane, allene, propyne, propene, acrolein, methyl propenoate, 1-butyne, propanal, 1,3-butadiene, trans-(2)-butene, cis-(2)-butene, and benzene) were also measured. They elaborated a detailed kinetic mechanism, that contains 301 species and 1516 elementary reactions. This mechanism allowed to understand the effect of the ester function on the combustion and the differences between the combustion of a saturated (methyl butanoate) and an unsaturated (methyl(E)-2-butenate) ester. They concluded that the combustion of unsaturated ester leads to the formation of higher levels of soot precursors than the saturated ester combustion.

The study of three unsaturated esters ($C_5H_8O_2$), methyl crotonate, methyl methacrylate and ethyl propenoate, has been investigated by Yang et al. [58] in 2011. The low-pressure premixed laminar flames have been stabilized on a McKenna burner at 2.67 kPa for the methyl crotonate and the methyl propenoate, and 4.0 kPa for the methyl methacrylate. The sampled gas was analyzed using a molecular beam mass spectroscopy. The temperature profiles were determined using laser-induced fluorescence (LIF) with the flame unperturbed by the sampling cone. The peak temperature for all the investigated flames was about 2100 K . All the main chemical species present good agreement

between the experimental and the simulated mole fraction profiles. Intermediate species analyzed in all the three flames are: CH_3 , CH_4 , C_2H_2 , C_2H_4 , C_3H_3 , C_3H_4 , C_3H_5 , C_4H_2 , C_4H_4 , C_6H_6 and CH_2O , CH_3OH , $\text{C}_2\text{H}_4\text{O}$, $\text{C}_2\text{H}_6\text{O}$, $\text{C}_3\text{H}_6\text{O}$. Compared to saturated esters flames, the authors observed a wider variety of heavy oxygenates in these unsaturated esters. These heavier oxygenated compounds are not formed only by H abstraction reactions, but also from the addition of radicals such as H , O , OH and CH_3 to the double bond in the fuel. In conclusion, the presence of the double bond in esters enhances the formation of oxygenated compounds during esters combustion at high temperature.

The methyl hexanoate ($\text{C}_7\text{H}_{14}\text{O}_2$) oxidation was studied in a jet-stirred reactor at 10 atm with a constant residence time of 1 s by Dayma et al. [59] in 2008. The temperature range used in the study was 500-1000 K for the lean, stoichiometric and rich conditions ($\phi = 0.5$, 1 and 1.5). A gas chromatography and a gas chromatography coupled with a mass spectroscopy (GC-MS) were used to identify and analyse the reactants, intermediate species and the products. The authors elaborated a kinetic model of methyl hexanoate combustion containing 435 species and 1875 reversible reactions. The detailed kinetic mechanism was validated by the experimental data reported in their study. It appeared that the combustion of methyl hexanoate is mainly controlled by the weakness of the $\text{C}-\text{H}$ bonds on the carbon 2 all over the studied temperature and pressure range. The last carbon near the ester function does not affect the reactions during the methyl hexanoate oxidation.

Very recently, in 2015, Dmitriev et al. [60] studied the effect of soot precursors in a rich premixed heptane (C_7H_{16})/toluene (C_7H_8) flame by adding methyl pentanoate ($\text{C}_6\text{H}_{12}\text{O}_2$) in the fuel composition. This premixed stabilized burner flame was investigated using molecular beam mass spectroscopy as an analysis technique for a single the equivalence ratio. The temperature profiles were measured using a S-type thermocouple (Pt/Pt + 10%Rh) with SiO_2 ant catalytic coating. The fuels, the oxidizer and the principal products such as H_2 , H_2O , CO and CO_2 present a very good agreement between the experimental and the simulated mole fraction profiles. The intermediate species analyzed in this work are: CH_4 , C_2H_2 , C_2H_4 , C_3H_3 , C_3H_4 , C_3H_6 + CH_2CO , C_4H_2 , C_4H_4 , C_4H_6 , C_4H_8 , C_5H_5 , C_6H_6 , $\text{C}_6\text{H}_5\text{OH}$ and $\text{C}_6\text{H}_5\text{C}_2\text{H}_3$. The addition of methyl pentanoate to the two rich flames reduced the mole fractions of

many intermediate species (C_3H_3 , C_2H_2 and C_6H_6) playing an important role in the formation of soot precursors (polycyclic aromatic hydrocarbons: PAH). However, the authors related that, when adding methyl pentanoate, there is no change in the concentration of the main radicals (H , O , OH and CH_3) that also contribute to soot precursors production. The other reasons of this reduction are: the reduction of toluene in the fresh gas composition that leads to the reduction of acetylene, propargyl radical and vinylacetylene, responsible for the formation of soot precursors (naphthalene).

In 2015, the characterization of methyl pentanoate ($C_6H_{12}O_2$) and methyl hexanoate ($C_7H_{14}O_2$) was investigated over a flat burner flame using a molecular beam mass spectrometry with tunable synchrotron vacuum ultraviolet (VUV) photoionization by Korobeinichev et al. [61]. For methyl pentanoate, two flames were investigated at atmospheric pressure and at two equivalence ratios (1.0 and 1.5). Two other methyl pentanoate flames were studied at these equivalence ratios at low pressure (20 Torr). For methyl hexanoate, at low pressure, two equivalence ratios (1.0 and 1.3) were used in their study. The authors provided new experimental data from the combustion of the two methyl esters. These experimental data were used to elaborate a new detailed kinetic mechanism validated on these experimental results. For the intermediate species, the agreement between the experimental and the simulated mole fraction profiles is good for some of them and a refinement of the other has to be performed.

In 2009, Dayma et al. [62] studied also experimentally in a jet-stirred reactor at 10 atm the oxidation of methyl heptanoate ($C_8H_{16}O_2$). The experimental conditions were: 0.7 s for the residence time, 550-1150 K for the temperature range and 0.6, 1 and 2 for the equivalence ratios. The initial fuel mole fraction concentration was 0.1%. For the analysis technique, they used a sonic probe connected via a Teflon heated line at 430 K to a gas cell for Fourier transform infrared (FTIR) analyses. Gas chromatography with capillary columns was used for stable species. To perform their analysis, they used also a gas chromatography coupled with a mass spectrometry (GC-MS). From the experimental data, they elaborated a detailed kinetic model containing 1087 chemical species and 4592 elementary reactions. The kinetic model predicts with good agreement the experimental data. As for the methyl hexanoate oxidation [59], the methyl heptanoate combustion is mainly controlled by the weakness of the $C-H$ bonds on carbon 2. The carbon 2 is the carbon in α -position of the

carboxyl function of the ester.

In 2010, Glaude et al. [63] studied also the oxidation of methyl esters such as methyl hexanoate ($C_7H_{14}O_2$), methyl heptanoate ($C_8H_{16}O_2$) and methyl decanoate ($C_{11}H_{22}O_2$) in a jet-stirred reactor to model their combustion. The authors investigated the three methyl esters combustion under stoichiometric conditions at a pressure of 1.06 *bar* for a residence time of 1.5 *s*. The temperature range used in their study was 500-1100 *K*. The fuel had a mole fraction of 0.0021 and was diluted in helium. The gas chromatography was used to identify O_2 , CO_2 , CO , CH_4 , acetylene, ethylene, ethane, propene, propane, acetaldehyde, 1,3-butadiene, 1-butene, 1-pentene and the sum of propanal and acrolein, which could not be separated in this equipment. They elaborated a detailed kinetic model containing 1251 species and 7171 elementary reactions. The kinetic mechanism predicts well the experimental data proposed in their study. Models generated for methyl esters from C_7 to C_{11} showed that these esters have close reactivity under similar conditions [59, 62, 63]. The authors also showed that the ester group has very little influence on the reactivity of large esters and they react very similar to *n*-alkanes.

In 2011, the methyl octanoate ($C_9H_{18}O_2$) oxidation was studied in a jet-stirred reactor and in an opposed-flow diffusion flame by Dayma et al. [64]. For the methyl octanoate oxidation in a jet-stirred reactor, the authors used these experimental conditions: pressure of 0.101 *MPa*, a temperature range of 800-1350 *K* and equivalence ratios from $0.5 < \phi < 2$. For the diffusion flame, pressure of 0.101 *MPa* was also used. CO and CO_2 were measured using none-dispersive infrared detection (NDIR). The gas chromatography was used for hydrocarbons (from C_1 to C_5) and oxygenated species (acetaldehyde, ethenol, formaldehyde and ketene). The detailed kinetic model proposed by the authors contains 383 chemical species and 2781 elementary reactions. This kinetic mechanism represents fairly well the experimental data at high temperature. Validations at low temperature and high pressure are needed.

In 2012, Dayma et al. [11] studied experimentally the ethyl valerate ($C_7H_{14}O_2$) combustion at high pressure (10 *atm*) in a jet-stirred reactor, and the laminar burning velocities in a spherical combustion chamber. Three equivalence ratios of 0.6, 1 and 2 were studied in the temperature range of 560-1160 *K*. To deter-

mine laminar burning velocities, the authors used a range of equivalence ratios (from $\phi = 0.7$ to 1.4) and pressure (1, 3, 5 and 10 *bar*). Gas chromatographs with capillary columns were used for off-line analyses. Products identification was performed using a gas chromatography coupled with a mass spectrometry (GC-MS). The mole fraction profiles of different chemical compounds present during the ethyl valerate oxidation in a jet-stirred reactor were measured by using Fourier transform infrared (FTIR) and gas chromatography. The following species have been measured: ethyl valerate, O_2 , CO, CO_2 , H_2O , CH_2O , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_4H_8-1 , CH_3CHO , 1,3- C_4H_6 , 2-propenal, propanal, butanal and ethyl propenoate. The authors reported that the experimental error for the valeric acid measurements was too important to take it into account in the kinetic model validation.

According to the experimental results, they elaborated a detailed kinetic mechanism containing 522 species and 2719 elementary reactions showing a good agreement with the experimental data. Ethyl valerate laminar burning velocities at 1, 3, 5 and 10 *bar* in a stoichiometric condition is a function of $P^{-0.28}$. They also reported that at low temperature, the ethyl valerate oxidation follows a similar scheme as for *n*-alkanes. Finally, the laminar ethyl valerate speed was found to be sensitive to reactions belonging to the $C_0 - C_1$ submechanism and involving H atoms. This mechanism has been validated at atmospheric and high pressure, its validation at low pressure will allow to improve this detailed kinetic mechanism.

The results of this study will be discussed in details in Chapter 4.

Finally, ethyl valerate is produced avoiding energetic processes from biomass which is a renewable and green material. This molecule is one of the esters with 7 carbon atoms and physicochemical properties similar to gasoline. For this reason, it can be used as a fuel in a spark ignition engine to alleviate traditional fuel problems. We propose to investigate its combustion at low pressure in order to understand in details, the formation and the consumption of all the intermediate species that could appeared during its combustion. At low pressure, radical reactions are promoting additional beta-scission reactions. To understand with good confidence a fuel combustion behaviour, it is useful to validate the kinetic mechanism at high pressure (real applications) and at low pressure to show the involvement of radicals such as H, O, OH and HO_2 in the combustion. Indeed, the formation of pollutants such as aldehydes and poly-

cyclic aromatic hydrocarbons (PAH) leading to the production of soot, can be investigated at low pressure due to the slow kinetic velocity of intermediate species. To attempt this main objective, it is useful to study a premixed flame at three equivalence ratios that can be found in real applications. These equivalence ratios are stoichiometric, lean and rich as the formation of radicals is not the same for each composition. To show the impact of this phenomenon on ethyl valerate combustion, three premixed flat flames will be investigated in order to show the role of these radicals in the formation and the consumption of species. This will further allow the validation of the elaborated ethyl valerate detailed kinetic mechanism at low pressure in comparison with its previous validity at high pressure.

Conclusion

Biofuels can be produced from biomass using thermochemical and biochemical processes. These fuels can be used in different industrial processes such as boilers, burners, furnaces and in automotive applications.

Their utilization can contribute to the diversification of the energy sources. As the total carbon balance is nearly null for biofuels combustion, they can be used to reduce the impact of pollutants compared to traditional fossil fuels. Second generation biofuels such as valeric esters (pentanoate radical) can be used in replacement of gasoline in spark ignition engine (methyl, ethyl and propyl valerates) and, in replacement of gasoil in compression ignition engine (butyl and pentyl valerates). These biofuels are synthesized from biomass using chemical processes such as hydrolysis, hydrogenation and esterification.

Esters (methyl and ethyl) have been studied in burners, jet stirred reactors and spherical combustion chamber to characterize their combustion at low and high pressure. Several kinetic mechanisms have been developed and are validated with the experimental data.

In this work, three ethyl valerate premixed flames will be stabilized on a burner at low pressure at different equivalence ratios in order to elaborate a new detailed kinetic model.

Chapter 2

Experimental setup

Introduction

To study one dimensional premixed flat flames at low pressure and to determine the mole fraction concentrations of each chemical species formed and consumed during the combustion, an experimental setup has been developed in this work. This chapter presents the experimental setup used to stabilize the low pressure ethyl valerate flames on the burner.

The structure of a laminar and one dimensional flame consists of an evolution in a single space coordinate (Z axis that is perpendicular to the surface of the burner) of fuel, oxidizer, intermediate and product species. A low pressure allows to analyse the profiles of each chemical species. Indeed, in this condition the chemical kinetics is slower and the flame is thicker.

However, working with esters requires some modifications of an existing test bench due to their high boiling point at atmospheric pressure. Indeed, the fuel must be blended to the oxidizer and the diluent before its entrance in the combustion chamber. The mixing can only be done in the gaseous phase.

The present experimental setup is composed of an evaporation system (EV), a combustion chamber (CC), a compression system (CS) and a gas chromatography (GC). Each part of the experimental setup is described in details. To measure the experimental temperature profiles of the studied flames, a thin thermocouple is inserted in the combustion chamber. The correction applied to the measured temperatures is also described.

Finally, the three inlet compositions of the ethyl valerate premixed flames are presented.

2.1 Complete test bench setup

The ethyl valerate flat flames have been stabilized at 55 mbar, on a movable Spalding-Botha burner of 8 cm in diameter [65, 66, 67, 68]. A conical quartz nozzle, with an angle of 45° near the tip, is facing the surface of the burner. At the tip, the hole diameter is 0.2 mm to allow the sampling throughout the flame.

Experimentally, the burner can be moved allowing to fix the sampling position. The position refers to the distance from the burner, at 0 mm, the burner is very close to the tip of the nozzle. Experimentally, we do not sample at this position because the burner is touching the nozzle. The first sampling position is located at 1 mm, for the fresh gases. The burner can be moved from 1 to 70 mm. However, the maximum position is 25 mm in these experiments. After this distance there is no more change in the flame composition.

The other parts of the burner will be described in the following sections where the complete setup is divided in four main parts: the evaporation system, the combustion chamber, the compression system and finally the gas chromatography. The complete schematic of the experimental setup is shown in Figure 2.1.

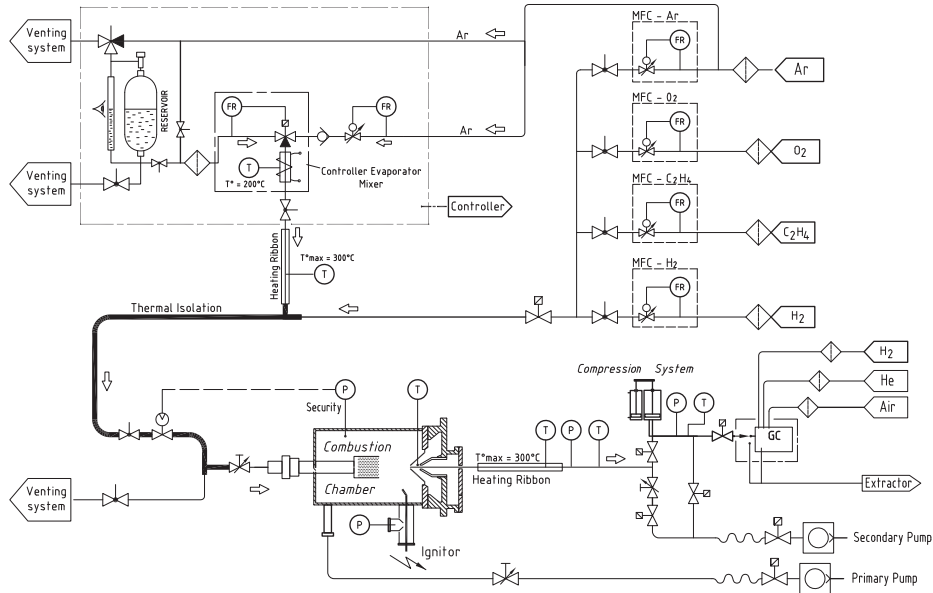


Figure 2.1: Schematic of the experimental setup.

2.2 Evaporation system

Ethyl valerate has a boiling point of 145°C at atmospheric pressure. To obtain a perfect gas mixture with the other gases (O_2 and Ar), an evaporation system has been added to the experimental setup.

The first challenge is to obtain a constant mass flow rate for the fuel during all experiments. This ensures the necessary stability of the flame during the performed experiments. The second challenge is to avoid any condensation before the combustion chamber to keep a constant flame composition.

The evaporation system, a setup composed of two mass flow controllers and an evaporator has been assembled (Figure 2.2).

A reservoir with a capacity of 1 l of liquid is put under pressure (3 bar) thanks

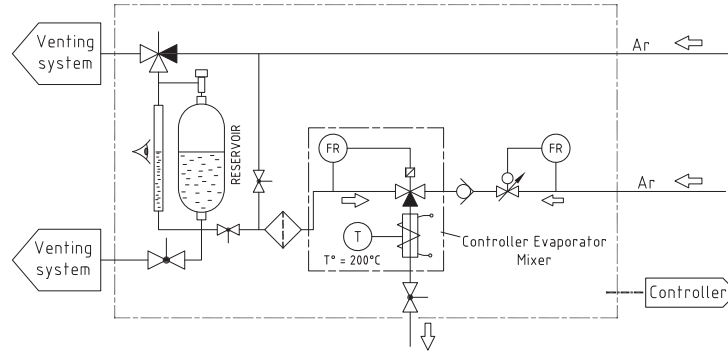


Figure 2.2: Complete scheme of the evaporation system.

to an argon supply at the top. At the exit of the reservoir, a controller sets the liquid mass flow rate, with a maximum rate of 110 g/h . To avoid impurities from the reservoir to pass through the mass flow controller, a filter is placed between the reservoir exit and the mass flow controller. A venting system is used after each filling of the reservoir, to avoid contamination by air of the ethyl valerate. This venting system is connected to a primary pump via the combustion chamber.

Right before the inlet of the evaporator, the ethyl valerate is mixed with argon used as a gas vector with a maximum rate of 2 ln/min . This argon flux is part of the diluent. To avoid impurities in the mixture (Ar - Ethyl valerate) a filter is also placed between this second mass flow rate controller and the argon bottle.

The evaporator is composed of a winding stainless steel pipe enclosed in a heated aluminium block. The evaporator temperature range is $30 - 200^{\circ}\text{C}$. For

the experiments, the evaporator set temperature is 180°C . To keep the evaporated mixture (Ar - Ethyl valerate) in an homogeneous gas state, a heated ribbon at 250°C is placed around the pipings between the evaporator and the combustion chamber.

Moreover, all the pipings are kept at low pressure (with a maximum pressure of 60 *mbar* during the experiments). These precautions help to prevent any condensation of fuel from the evaporator exit to the combustion chamber entrance.

2.3 Combustion chamber

At the inlet of the burner, the gas mixture ($\text{C}_7\text{H}_{14}\text{O}_2 - \text{Ar} - \text{O}_2$) is kept at 90°C (at low pressure) using water circulating around the moving part of the burner. The combustion chamber is connected to a primary vacuum pump to maintain the low pressure condition required by the experiments. During the experiments, the combustion chamber has been maintained at 55 *mbar* while the pressure was 20 *mbar* behind the nozzle. This difference of pressure between the combustion chamber and the nozzle, allows to control the sampling of the gases. To keep the sampled gas at high temperature and to avoid condensation of the fuel or others species, a heated ribbon at 200°C is used after the nozzle until the compression system.

As the combustion is exothermic, a cooling water system is used around the combustion chamber and the quartz nozzle. The conditions are not adiabatic and the temperature profile must be measured, experimentally, throughout the flame.

The combustion chamber contains also an igniter in the bottom part. This igniter is movable and can be introduced in the combustion chamber facing the gas inlet. After the ignition of the premixed gases, the igniter is moved to the lower position to avoid a contact with the burner surface.

Working with gases, implies some security precautions. The combustion chamber has a security automatic pneumatic valve (working at 8 *bar*) controlled by a pressure sensor. When the pressure reaches 100 *mbar* in the combustion chamber, the automatic valve closes the gas inlet. Another security automatic valve is placed before the combustion chamber. This valve opens only if the cooling water system is opened. With these precautions, experiments can be safely performed. The start-up procedures of the test bench is presented in

Appendix CD.

2.4 Compression system

As the experiments have been performed at low pressure (55 *mbar* in the combustion chamber and 20 *mbar* after the quartz nozzle) and as the gas chromatography is working at atmospheric pressure, an in-line compression system is needed to increase the pressure of the collected gases before their injection in the gas chromatography (Figure 2.3).

The system must be in-line to prevent any condensation of the fuel and other

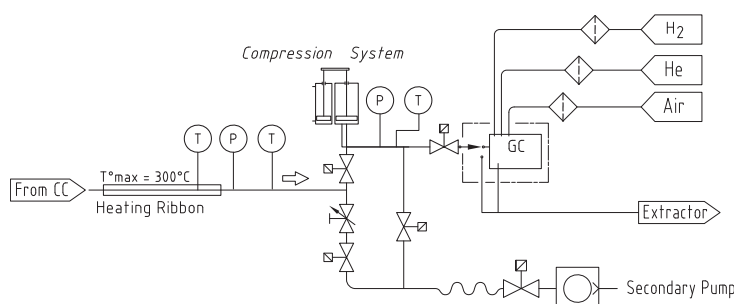


Figure 2.3: Complete schematic of the compression system and the gas chromatography.

chemical compounds. The compression system is composed of a cylinder and a piston with a displacement of 2 litres. While the pressure after the nozzle is kept at 20 *mbar*, it is temporally raised up to 40 *mbar* to introduce a sufficient amount of gas in the sampling cylinder, by stopping the pumping with the secondary pump. When this pressure (40 *mbar*) is reached in the sampling cylinder, an automatic valve closes and the pumping starts again to evacuate the collected gases from the combustion chamber through the nozzle. After compression, the pressure rises up to 2431 *mbar* to have sufficient amount of gases in the pipes from the sampling cylinder to the gas chromatography valve. The volume of the sampled gas is 2006 *ml* before compression and 33 *ml* after it. The compression is nearly isothermal with a regulated heated ribbon at 130°C placed around the cylinder.

The pressure and the temperature conditions are set to avoid condensation. However, we observed experimentally some ethyl valerate condensation between the compression system and the gas chromatography. This condensation is observed when the ethyl valerate concentration remains high, i.e. when sam-

pling is taken in the fresh gases. This condensation could be due to the rapid expansion of the gases to bring them to atmospheric pressure before their injection into the gas chromatography. The compression system parameters are summarized in Table 2.1.

Table 2.1: *Compression system.*

<i>Step</i>	Pressure (<i>mbar</i>)	Temperature ($^{\circ}C$)	Volume (<i>l</i>)
Start of compression	40	70.6	2.006
End of compression	2431	71.9	0.033

Ethyl valerate condensation affects slightly the mass balance in the fresh gases (Chapter 4). We assume that there is no chemical reaction during the compression, due to the low temperature and low concentration of each species in the sampled gas, and due to the rapid compression.

Note that this system is controlled automatically via the *EzChrom*® software. Automatic valves are placed before and after the compression system. The valves are working in the following way (Figure 2.4):

1. at the first step, the valve V6 is opened to create vacuum condition in the sampling cylinder. Then, the first 2-way automatic V5 valve (placed between the cylinder and after the nozzle) is opened allowing to collect the sample, while the second V5 is closed. This second V5 valve is in-line with the secondary vacuum pump. These two valves are working in opposition, if the first is opened, the second is closed and vice versa.
2. when the pressure reaches 40 *mbar* in the cylinder, the first V5 valve is closed, then the second V5 valve is opened to continue the evacuation of the burned gas.
3. V6 valve closed automatically to allow compression of the collected gas.
4. after the compression, another 2-way automatic valve (V7) placed in-line with the gas chromatography, is opened to expand the compressed gas. This gas expansion is done until the pressure reaches atmospheric condition.
5. Finally, the GC's valve (E2) is opened to collect the sample. After this sequence, the V8 valve is opened to evacuate the rest of gases from the

compression system to the secondary pump.

To control the temperature and pressure before and after the compression, different thermocouples and pressure sensors are placed in the system as represented by the P and T symbols in Figure 2.4.

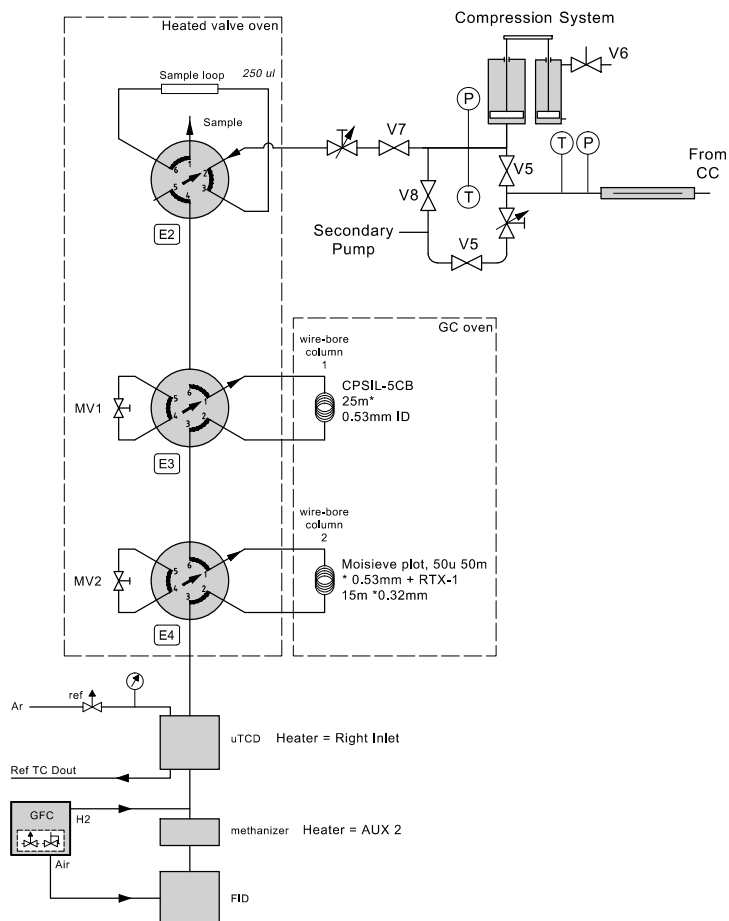


Figure 2.4: Schematic illustrating automatic valves used for the compression system and the gas chromatography.

2.5 Gas chromatography

To analyze different stable chemical compounds formed during the combustion of ethyl valerate, a gas chromatography is used as the analysis method. The choice of columns should be adapted to the chemical structure of the analysed

molecules.

This analysis method consists in using a vector gas called the "mobile phase" (H_2 , Ar, He, N_2 , CO_2) mixed with the sampled gas, passing through capillary columns (stationary phase). The separation between the different species in gases is based on their molecular weight, their chemical affinity with the chemical structure of the stationary phase (polarity properties). The oven temperature, the flow rate of the vector gas and the nature of the vector gas are used to improve the separation of the chemical compounds in the sampled gas.

The response of the separated and identified chemical compounds appear as peaks using the *Ezchrom*® software, with a specific retention time for each species.

The gas chromatography used in this work is a TOGA/Trace GC. The gas sample collected through the flame is analyzed in the gas chromatography composed of three capillary columns: CP SIL 5CB for hydrocarbons and oxygenated compounds and Molsieve for permanent gases in series with RTX1 for the analyzed gas flow rate restriction before passing through the micro-TCD (see in Figure 2.4).

There is an automatic valve before each column that allows choosing the column in which the gas sample can be separated.

1. E2 allows the introduction of the sample into the columns
2. E3 allows to use the CPSIL 5CB column for separation of the collected gas
3. E4 is used for the Molsieve and RTX-1 columns

When E3 is opened, the sample can be analyzed in the CPSIL 5CB column, while closing it, the sample by-passes this column. Then, if E4 is opened, the sample can be analyzed in the Molsieve and RTX-1 columns, while closing it, this column is by-passed. If the two valves are opened, the sampling gas will be separated firstly in the CPSIL 5CB column, then in the Molsieve and RTX-1 ones. While closing both valves, there is no separation during the analysis.

The columns characteristics are presented in Table 2.2. H_2 , O_2 , Ar, CO_2 are present in the flame composition, we used He as the vector gas. With He as gas vector, the separation between argon and oxygen is not possible. Then, we also used argon as vector gas to separate these two gases (O_2 and Ar).

Table 2.2: Characteristics of the columns used in the gas chromatography.

Column	length (<i>m</i>)	Internal diameter (μm)	External diameter (<i>mm</i>)	Maximum temperature $^{\circ}C$
CP-SIL 5CB	25	5	0.53	350
HP-MOLSIEVE	30	50	0.53	300
RTX-1	15	0.1	0.32	350

2.5.1 Injection chamber

The injection chamber is a part of the GC where valves and the injection system are placed. To improve the experiment in minimizing the condensation effect of samples after compression, the temperature is regulated at $110^{\circ}C$. This is the maximum temperature allowed by the GC in this zone. All valves are automatic.

2.5.2 Gas flow rate

The flow rate of the vector gas is constant and controlled by the GC in terms of pressure sets to 2.5 *bar* for all the experiments and for all the vector gases used .

2.5.3 Oven

In our work, the oven of the GC contains the three columns and its temperature sequence is programmed as depicted in Table 2.3. Using the gas chromatography as an analysis technique, the oven temperature, the volume flow rate and the nature of the vector gas can be used to improve the separation between the different species of the analyzed mixture [69, 70, 71, 72].

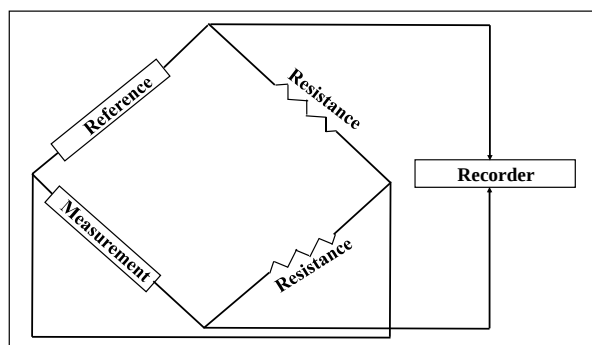
Two detectors (TCD: thermal conductivity detector and FID: flame ionization detector) are used to detect the signals when a compound goes out the capillary column. These detectors are placed in series. The FID detector is more sensitive than the TCD detector. Hydrocarbons and oxygenated compounds are detected at this detector but not permanent gases such as O_2 , H_2 , H_2O , ...due to the fact that there is no C-H bonds in their chemical formula.

Table 2.3: Programmed temperature sequence in the oven.

	Oven rate (°C/min)	Temperature (°C)	Hold time (min)
Initial		40	7.00
Ramp 1	80	65	10.00
Ramp 2	10	120	5.00
Ramp 3	40	40	10.00
Ramp 4	120	90	9.57
Ramp 5	50	250	22.00
Ramp 6	100	90	3.40

2.5.4 Thermal conductivity detector (TCD)

Chemical compounds have different thermal conductivities. This property is used in GC, via a Katharometer called "Thermal Conductivity Detector" (Figure 2.5). The analysis consists on the difference of conductivities established between the reference compound (vector gas) and the analyzed one. When the vector gas passes through the TCD, its conductivity is taken as reference (0 volts). When another compound passes through this detector, the difference between its conductivity and the gas vector one is observed, a peak appears according to the concentration of the analyzed compound. The TCD is a universal

**Figure 2.5:** Simplified schematic of a Thermal Conductivity Detector.

detector : every chemical compound can be detected. The only parameter that has to be taken into account is the difference of conductivity between the analyzed compound and the vector gas. This detector is also non destructive but

not very sensitive.

In our work, the temperature set for the TCD box is 180°C and the filament is regulated at 280°C . The sampling rate is regulated at 50 Hz (frequency), its gain is 2. The gain is defined as the ratio between the signal and the noise. Due to the temperature sequences in the oven, the overall running time is 80 min for the method used.

The thermal conductivity detector's signal is expressed in microvolt (μV).

2.5.5 Flame ionisation detector (FID)

The electrical conductivity of a flame burning with a mixture of hydrogen and oxygen (in air: $\text{O}_2 - \text{N}_2$) is very affected by the vapours of organic chemical compounds. This effect is used for the detection of organic substances in gas chromatography [73]. A mixture of H_2 - air is burned in the FID (Figure 2.6). The electric conductivity is modified by the presence of other chemical compounds. This modification is proportional to the concentration of the substance in the sampled gas. This method is destructive and the burned separated compound cannot be used latter. For this reason, the FID is always the last detector. The intensity of the peak is expressed in picoAmpere (pA).

The hydrocarbons, oxygenated species, carbon monoxide and carbon dioxide

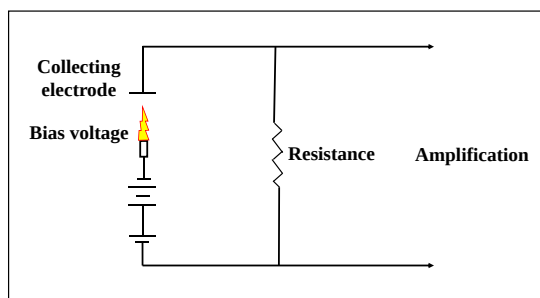


Figure 2.6: Simplified schematic of a Flame Ionisation Detector.

are analyzed using the FID detector. The others permanent gases such as O_2 , H_2 , Ar and H_2O are analyzed using the TCD detector.

In our work, the volume flow rate is 350 and 70 ml/min for the air and hydrogen, respectively. To have a good resolution with peaks, a make up of the vector gas (He) is used and set at 25 ml/min . This flow rate of the vector gas allows to increase the ratio signal/noise and then, increases the peak's signal

response. Other parameters regulated at FID are the base temperature that is set at 330°C and the ignition threshold at 1.0 pA .

2.5.6 Methanizer

This gas chromatography has the particularity of being equipped with a methanizer (Figure 2.4), that allows converting carbon monoxide (CO), carbon dioxide (CO_2) and formaldehyde (CH_2O) into methane (CH_4). This is due to the reduction reactions (heterogeneous catalyst reactions on a solid support such as nickel) between these molecules and hydrogen in the methanizer. The CO , CO_2 and CH_2O FID signals are thus CH_4 detected peaks but the retention times correspond to the initial species thanks to the chromatographic columns. The advantage of this technique is for the calibration: only methane or one of these species can be used. Therefore, the experimental errors on CO , CO_2 and CH_2O concentrations are reduced due to the higher sensitivity of FID compared to TCD one. This is valid for the FID signal only because the methanizer is placed after the TCD detector and before the FID.

2.5.7 Valve sequence

To improve the separation between different stable chemical compounds produced during combustion, automatic valves are used. These valves allow to control the compression system, the injection system in the GC and the different columns used during the analysis.

In our work, the valve sequences in the GC are depicted in Table 2.4. At the beginning of a measurement, all the column valves are opened by default ($E3$ for the CPSIL 5CB and $E4$ for the molsieve and RTX-1 columns).

2.5.8 Identification of species

The analyzed stable chemical compounds are presented in Table 2.5 with their retention times, according to the temperature program of the oven (Table 2.3). To determine the retention time of each analyzed species, each pure chemical substance was injected in the columns. With this temperature program, the separation between species is good.

Table 2.5 shows the species chemical names and structures, the column in which they have been separated, the vector gas used, the detector and their

Table 2.4: Valve sequences in the GC programmed with EzChrom® (Valves E3 and E4 opened by default).

Valve	Action	Time (min)	Comments
E ₈	ON	0.01	cleaning of the CS
E ₈	OFF	0.04	ending of the CS cleaning
E ₆	ON	0.05	opening of the sampling cylinder
E ₅	ON	0.06	filling of sample in the cylinder
E ₅	OFF	1.00	ending of sample in the cylinder
E ₆	OFF	1.02	closing of the sampling cylinder
E ₇	ON	1.07	expansion of the compressed sample
E ₂	ON	1.09	opening of the GC sampling valve
E ₂	OFF	1.19	closing of the GC sampling valve
E ₇	OFF	1.20	ending of the sample expansion
E ₄	ON	3.41	closing of the molsieve column
E ₆	ON	10.00	beginning of the rest gas compression
E ₆	OFF	12.00	ending of the rest gas compression
E ₇	ON	12.50	cleaning of the CS
E ₇	OFF	15.00	ending of the CS
E ₄	OFF	30.00	opening of the molsieve column
E ₃	ON	30.00	closing of the CPSIL 5CB column
E ₈	ON	40.00	cleaning of the CS
E ₈	OFF	42.00	ending of the CS cleaning

retention time, respectively.

Figure 2.7 shows a chromatograph obtained via the TCD detector using EzChrom® software, for a rich ethyl valerate flame at 6 mm.

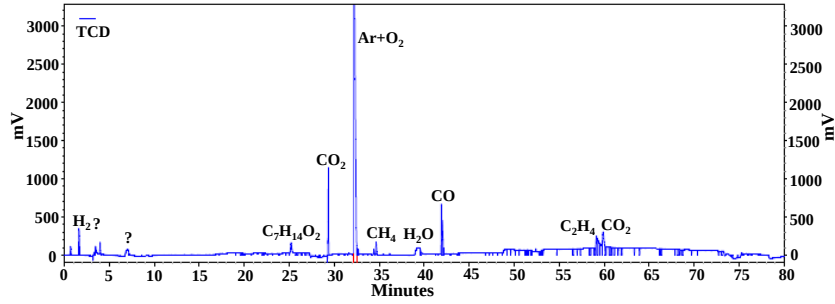
Figure 2.8 illustrates a chromatograph obtained via the FID detector using EzChrom® software, for a rich ethyl valerate flame at 6 mm. Thanks to the Table 2.5, the identification of the peaks can be performed.

2.5.9 Calibration of the gas chromatography

Peaks obtained via the Ezchrom® software for different stable chemical species have to be expressed in terms of mole fractions. To convert FID and TCD signals (in pA and μ V respectively) into mole fractions, a calibration of each species must be performed.

Table 2.5: Species analyzed by gas chromatography.

Species	Formula	Column	Vector gas	Detector	Retention time (min)
Formaldehyde	CH ₂ O	CPSIL5CB	Helium	FID	3.7
Acetaldehyde	CH ₃ CHO	CPSIL5CB	Helium	FID	4.4
Formic acid	HOCHO	CPSIL5CB	Helium	FID	6.4
Acetone	CH ₃ COCH ₃	CPSIL5CB	Helium	FID	6.7
Valeric acid	C ₄ H ₉ COOH	CPSIL5CB	Helium	FID	9.9
Ethyl valerate	C ₇ H ₁₄ O ₂	CPSIL5CB	Helium	FID	25.2
Carbon dioxide	CO ₂	CPSIL5CB	Helium	FID	30.0
Carbon dioxide	CO ₂	Molsieve	Helium	FID	60.2
Methane	CH ₄	Molsieve	Helium	FID	37.4
Carbon monoxide	CO	Molsieve	Helium	FID	43.3
Ethylene	C ₂ H ₄	Molsieve	Helium	FID	61.7
Acetylene	C ₂ H ₂	Molsieve	Helium	FID	71.1
Argon	Ar	Molsieve	Helium	TCD	33.2
Water	H ₂ O	Molsieve	Helium	TCD	38.8
Oxygen	O ₂	Molsieve	Argon	TCD	5.9
Hydrogen	H ₂	Molsieve	Argon	TCD	5.4

**Figure 2.7:** TCD chromatograph of ethyl valerate rich flame at 6 mm from the burner surface (intensity (μV) versus retention time (min)).

For calibration, bottles containing mixture gases at different concentrations are used for all permanent gases: ethylene, methane, acetylene, H₂, O₂ and Ar. These graphs present the mole fraction versus the signal intensity (Figures 2.9, 2.10 and 2.11). The example of a calibration curve obtained for H₂ is presented in Figure 2.9.

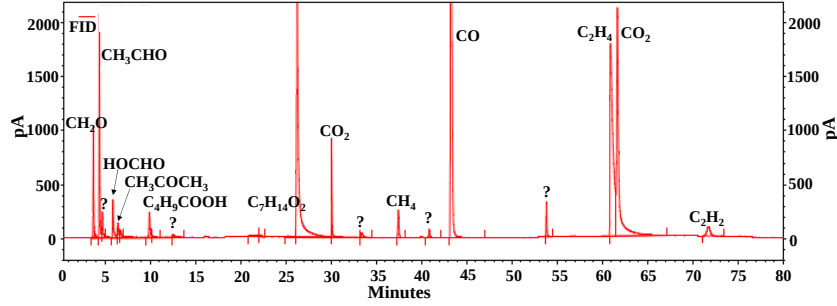


Figure 2.8: FID chromatograph of ethyl valerate rich flame at 6 mm from the burner surface (intensity (pA) versus retention time (min)).

For methane, the calibration is presented in Figure 2.10 For the liquid com-

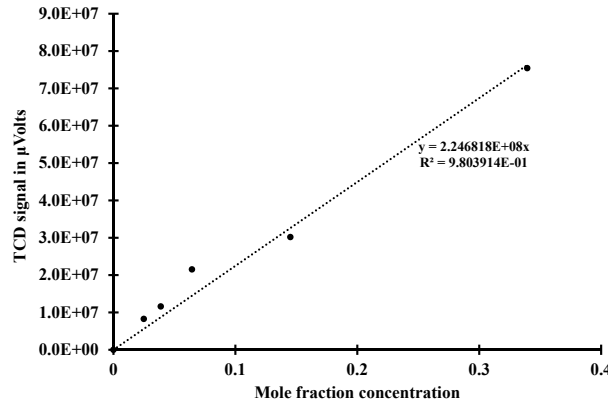


Figure 2.9: Calibration curve of hydrogen obtained via TCD signal.

pounds, the Antoine's Equation (2.1) is used to determine the saturated pressure of each species at 22°C. The perfect gas law (Equation (2.2)) is used to determine the mole number and the mole fraction in 2.5 ml (volume of the sampling bottle). The obtained mole fraction (Equation (2.3)) is diluted at different levels to obtain different mole fractions. With these data, we obtain a calibration curve for each species.

$$\log P = A - \frac{B}{T + C} \quad (2.1)$$

Where : A, B and C are the Antoine constants; P (pressure in bar) and T (temperature in Kelvin).

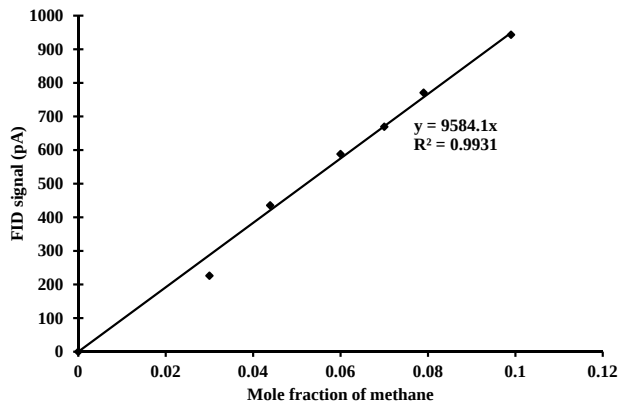


Figure 2.10: Calibration curve of methane obtained via FID signal.

$$n_i = \frac{PV}{RT} \quad (2.2)$$

With : n_i (mole number of species i in mole), P (pressure in Pascal), V (volume in m^3), T (temperature in Kelvin) and R (perfect gas constant: 8.314 J/mol.K).

$$X_i = \frac{n_i}{n_t} \quad (2.3)$$

X_i is the mole fraction of the species i and n_t the total number of moles (the total mole number is determined at atmospheric pressure, where n_i is calculated from Antoine equation).

An example of a calibration obtained with this method (formic acid) is presented in Figure 2.11.

For chemical compounds having the same chemical function such as acetaldehyde-formaldehyde and formic acid - valeric acid, the experimental calibration curves normalized to one carbon atom have been compared. Indeed, the ratio between the experimental calibration curve of these species is compared to the effect of the number of carbon atom. If this effect is quite similar, this factor can be used instead of doing multiple calibrations for compounds having the same chemical function and for species that are not very stable [74].

In our case, this effect was observed only for carboxylic acid function. For this reason, we calibrated separately each species formed during ethyl valerate combustion, except for the carboxylic acid function such as formic acid, acetic acid and valeric acid. For this chemical function, the observed results show that the

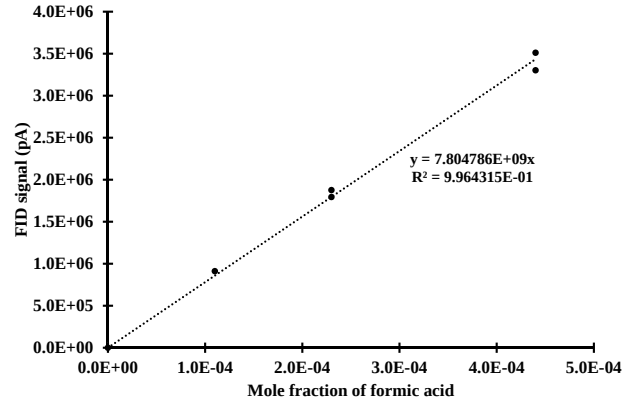


Figure 2.11: Calibration curve of formic acid obtained via FID signal.

effect of the increase of the number of carbon atoms has a proportional effect on the increase of their FID signals.

To test the reliability of the methanizer, some experiments have been performed. The ratios between CO/CH_4 and CO_2/CH_4 was determined using FID signals. If this ratio is constant as in the bottles, it means that the conversion due to the methanizer is also constant for CO , CO_2 and CH_2O . We use two bottles with different mixtures and concentrations of these species (methane, carbon monoxide and carbon dioxide).

Table 2.6 shows the comparison between the signals to assess the conversion capacity of the methanizer. The results shown in Table 2.6 prove that the meth-

Table 2.6: Comparison between the FID and TCD signals to assess the methanizer conversion.

Species	FID (pA)	TCD (μVolts)	Reference bottle (%)
CO	109351824	3411709771	25.36 ± 0.51
CO_2	42673415	1166147923	10.12 ± 0.20
CH_4	17069366	917373783	3.972 ± 0.079
CO/CH_4	6.40	3.71	6.38
CO_2/CH_4	2.50	1.27	2.55

anizer has a good repeatability in the conversion of CO and CO_2 into CH_4 . In the reference bottle, the CO/CH_4 ratio is 6.38 against 6.40 for measured FID

signals. For the second ratio between CO_2/CH_4 , this ratio is 2.55 in the reference bottle and 2.50 based on the FID signals. Based on these results, we note that the conversion yield of the methanizer leads to the same ratio as in the reference bottles. Therefore, the methanizer has good chemical conversion of CO and CO_2 into CH_4 . For CH_2O , the same effect is assumed. Formaldehyde is in liquid form. It is not possible to mix it with methane, carbon dioxide or carbon monoxide to check its conversion yield. For this reason and due to the fact that CH_2O is more reactive, we used the calibration line of CH_4 for this molecule taking into account that the conversion yield in the methanizer is the same while calibrating and when using the Antoine equation.

Moreover, we observe a difference between the ratios with the TCD detector. This is due to the fact that TCD is placed before the methanizer (Figure 2.4). The standard deviation for this analysis is estimated at 2%. These results are the average of three values from three experiments in the same condition of pressure (1.1 *bar* regulated at the bottle regulator).

2.5.10 Conversion of GC signal into mole fraction

To convert the numerical values (intensity of peak) into mole fraction, Equation (2.4) is used:

$$X_i = \frac{Y_i}{a} \quad (2.4)$$

Where Y_i presents the experimental integration surface for species i as depicted in Figures 2.9 and 2.10 obtained via TCD or FID detector, a is the slope of the equation (Table 2.7) and X_i the mole fraction of the investigated species i .

Table 2.7 shows the values of the equation obtained from the calibration curve of each species.

2.5.11 Experimental error

Different parameters such as the sensitivity of the gas chromatography, the reproducibility of the results, the calibration and the stability of the analyzed molecules, the pressure and the mass flow rate can be taken into account in the determination of the experimental uncertainties. These uncertainties are the sum between the uncertainty due to the calibration and the standard deviation calculated for each species to check the reproducibility of the measured values. It is noted that the calibration should not affect substantially the error due to the high correlation coefficient of the linear regression. This coefficient

Table 2.7: Calibration slope of the analyzed species.

Species	Formula	Equation's slope a	Correlation coefficient R^2	Calibration curve
Acetaldehyde	CH_3CHO	25943.6	0.94	CH_3CHO
Acetylene	C_2H_2	28757.1	0.98	C_2H_2
Acetone	CH_3COCH_3	61067.8	0.98	CH_3COCH_3
Argon	Ar	3689.3	0.99	Ar
Carbon dioxide	CO_2	9584.1	0.99	CH_4
Carbon monoxide	CO	9584.1	0.99	CH_4
Ethylene	C_2H_4	2323	0.99	C_2H_4
Ethyl valerate	$\text{C}_7\text{H}_{14}\text{O}_2$	4793.2	0.92	$\text{C}_7\text{H}_{14}\text{O}_2$
Formaldehyde	CH_2O	9584.1	0.99	CH_2O
Formic acid	HOCOH	78047.3	0.99	HOCHO
Hydrogen	H_2	2246.8	0.98	H_2
Methane	CH_4	9584.1	0.99	CH_4
Oxygen	O_2	357.8	0.99	O_2
Valeric acid	$\text{C}_4\text{H}_9\text{COOH}$	3900236.5	0.99	HOCHO

is the square of the product moment of the correlation coefficient (R^2). For molecules having low concentrations, this correlation coefficient can be affected by the error that could be estimated at 5%. These lines of calibration should remained similar during all the experiments. Due to this observation, the calibration is a low source of error for the measurement of the mole fractions for high concentrations (high than 0.01) and is a slight source of errors for low concentrations (less than 0.01).

Thanks to the calibration and the validation steps, the experimental error is estimated at 5% for the main species (reactants and products) such as O_2 , CO_2 , CO and H_2O considering that 1% of this uncertainty is from the calibration curve and 4% calculated from the measured values (standard deviation). For species such as H_2 and EPE, it is estimated at 10% (5% for the calibration curve and 5% for the measurement). We note for these two species that even their maximum concentrations are higher than 0.01, H_2 is more difficult to measure due to the diffusion effect and EPE due to the condensation effect. For the other intermediate species, the experimental error is 20% for CH_3CHO , CH_2O , C_2H_4 and CH_4 . Finally, for $\text{C}_4\text{H}_9\text{COOH}$, CH_3COCH_3 , HOCHO, and

C_2H_2 , it is estimated at 25% due to their low concentrations for the first three chemical compounds and the non-sensitivity for the last one. The high percentage for the intermediate compounds is the sum of 5% from the calibration and 15 or 20% estimated due to the measured values obtained at the maxima of the concentration profile. This is also due to the sensitivity of the GC. It is more sensitive for high concentrations than low concentrations (< 0.001). The absolute uncertainty of the mass flow controllers is 0.05 % and the calculated one from the standard deviation obtained from six values sampled during 6 different days is 0.78 %. The total absolute uncertainty of the flow rate is the sum between the two and it is 0.83 %.

2.5.12 Nozzle effect to the measurements

The composition of the premixed flat flame is obtained by sampling the chemical compounds along the flame. In our study, a quartz nozzle is placed facing to the burner surface to allow sampling. This technique disrupts the flame because it is intrusive.

Struckmeier et al. [75] studied the influence of the nozzle on the temperature and on species concentrations in molecular beam mass spectroscopy flat premixed low pressure flames. They compared four different nozzles having different opening angles as shown in Table 2.8. The authors observed by com-

Table 2.8: Sampling nozzle configurations [75].

Opening angle	Tip diameter d (μm)	Height (mm)	Base diameter (mm)
25°	375	67.7	30
45°	50, 125, 325, 375, 475, 600, 700	50.5	40
65°	375	31.4	40
85°	375	25.6	45

paring different results from each type of nozzle that: for 85° nozzle, the studied profiles are shifted by 2.5 - 3 mm relative to the 25° one. For the 65°, shifts are 0.5 - 1.6 mm , and finally 0.2 - 1 mm for the 45° nozzle compared to the 25° nozzle. They mentioned that stable species are less perturbed than reactive ones, and shifts should be especially pronounced if the recombination of species is fast. If the species is easily produced or consumed by surface reactions, the

same phenomenon is observed.

In our study, we used a quartz nozzle with an angle of 45° and a hole tip diameter of 0.2 mm . This tip hole diameter was chosen to increase the quantity of sample that could pass through the nozzle. The compression system cylinder has a volume of 2 litres, as described before. To fill it rapidly, the tip hole diameter of the nozzle has to be taken into account. For the gas chromatography analysis, the hole diameter at the tip of the nozzle has to be larger than for the molecular beam mass spectroscopy. For the molecular beam mass spectroscopy, the sample is analyzed at very low pressure (10^{-7} mbar). However, for the GC, the pressure of the sampled gas must be increased up to the atmospheric pressure. A tip hole diameter of 0.1 mm was used by different authors using molecular beam mass spectroscopy [66, 67, 68, 76].

The effects of a sampling quartz nozzle on the flame structure of a fuel-rich low pressure propene flame were also been investigated by Hartlieb et al. [77]. They concluded that the shift of the concentration profiles of chemical species differed by more than an order of magnitude.

Due to these works on the quartz nozzle perturbation, in our work, using a quartz nozzle of 45° with a hole of 0.2 mm at its tip, a deviation of 1 mm in the concentration profiles could be attributed to the nozzle effect.

2.6 Flame temperature profile measurements

The experimental measurement of the flame temperature profile is necessary for the numerical simulations. Indeed, if the energy equation is solved by the software, the result will give the adiabatic temperature.

Many methods have been proposed to measure the temperature in a reactive zone, intrusive methods [75, 77], or, non intrusive methods using a laser [78].

2.6.1 Temperature measurement

In this work, we use a type B thermocouple composed of a mixture of platinum and rhodium in these proportions : PtRh6% - PtRh30%. The platinum and the rhodium have excellent thermal properties and their fusion temperature is 2045 and 2233 K , respectively. The thermocouple has a two branches of 0.1 mm of diameter connected in the center with a laser welding. Each branch of 0.1 mm is connected to another of 0.35 m in length with the diameter of 0.5 mm .

The platinum catalytic effect can increase the temperature on the thermocouple surface in contact with radicals. This effect can cause large uncertainties during the temperature profile measurement.

Kent [79] proposed, in 1970, to cover the thermocouple with a refractory material. This technique is used in this work and consists on depositing a ceramic layer material ($\text{BeO} - \text{Y}_2\text{O}_3$) on the surface of the thermocouple to prevent a platinum effect on the radicals produced during the combustion. The layer is available as a chlorhydric acid solution in which 7% of BeO (Berellium oxide) and 93% of Y_2O_3 (Yttrium oxide) are blended at 100°C . This acid solution is applied on the surface of the thermocouple and dried with a Bunsen flame several times until reaching a thickness of 0.12 mm .

Figure 2.12 shows the coated thermocouple used in the temperature measurements.

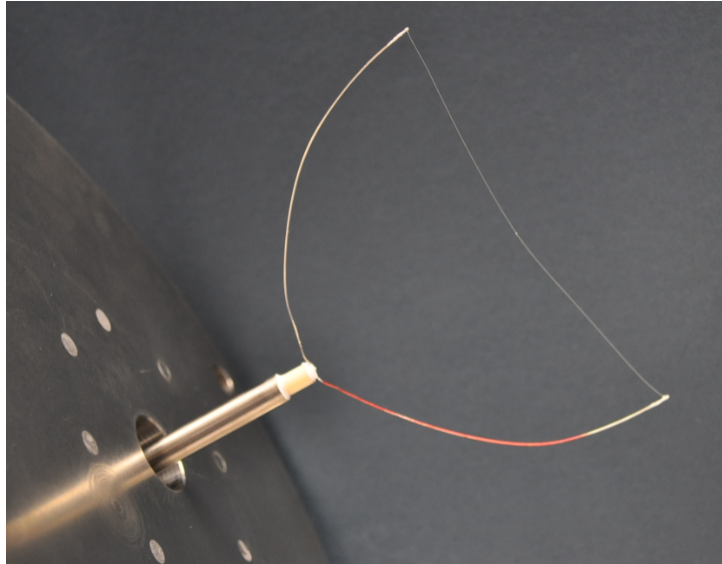


Figure 2.12: Coated thermocouple used in the temperature profile measurements.

2.6.2 Correction of the measured temperature

At high temperatures, the thermocouple loses energy by radiation. This heat loss is very important at high temperatures ($>1000\text{ K}$) and is unavoidable [80]. With radiation, the measured temperature is lower than the real one; a correction must be applied in this case.

Around the thermocouple, different ways of heat exchange are:

1. convection between the gas and the thermocouple (Q_{conv}),
2. thermocouple radiation (Q_{rad}),
3. catalytic recombination reactions with the thermocouple (Q_{cat}),
4. conduction along the thermocouple (Q_{cond}).

At equilibrium, all these fluxes are :

$$Q_{conv} + Q_{rad} + Q_{cat} + Q_{cond} = 0 \quad (2.5)$$

As the diameter of the wire is 0.12 mm, the conduction losses are negligible at the junction. Moreover, the thermocouple is parallel to the burner surface reducing the gradient.

The principal heat exchanges between the flame and the thermocouple are by radiation and convection:

$$Q_{conv} = h\pi d(T_g - T_c) \quad (2.6)$$

$$Q_{rad} = \epsilon\pi\sigma d(T_0^4 - T_c^4) \quad (2.7)$$

where:

1. h: convection heat exchange coefficient ($W.m^{-2}.K^{-1}$)
2. d: junction diameter (m)
3. ϵ : thermocouple emissivity coefficient
4. σ : Stephan - Boltzmann constant ($W.m^{-2}.K^{-4}$)
5. T_0 , T_g , T_c are the temperature (in Kelvin) of the burner walls, gas and thermocouple, respectively.

From Equation 2.5, the heat balance is reduced to :

$$Q_{conv} + Q_{rad} = 0 \quad (2.8)$$

Then, we have from Equations 2.6, 2.7 and 2.8:

$$h(T_g - T_c) = \epsilon\sigma(T_c^4 - T_0^4) \quad (2.9)$$

The corrected temperature value is determined by a measurement of T_c that allows to estimate T_g . Bonne et al. [80] proposed a method in which an electric compensation is used to evaluate the correction (Figure 2.13). This measurement consists to an injection of different electric powers to heat up the thermocouple and measure T_0 .

This method allows to determine the temperature gap between the real temperature (T_g) and the measured temperature (T_c). It consists in comparing the thermocouple readings in the flame and in vacuum while a high frequency (8000 Hz) alternative current is passing through the thermocouple (Figure 2.13). Firstly, different currents are injected in the thermocouple placed in

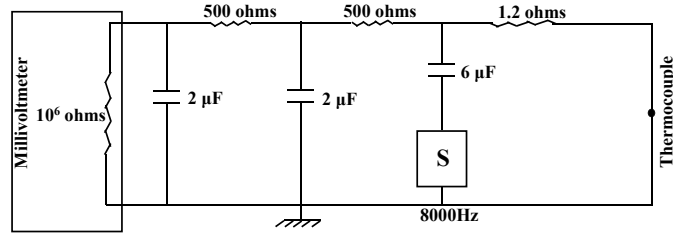


Figure 2.13: Electrical setup used for the electric compensation method [81].

vacuum in the combustion chamber. For each current a temperature is read from the thermocouple. A curve $I^2 = f(T)$ is obtained.

Secondly, in the presence of the flame at low pressure, the same operation is performed at different distances from the burner to obtain other curves ($I^2 = f(T)$).

In the vacuum, there is no convection and the electric energy provided to the thermocouple is equal to the radiation losses.

$$(RI^2)_{vacuum} = \epsilon\sigma\pi d(T_c^4 - T_0^4) \quad (2.10)$$

Where R is the thermocouple resistance per unit of length.

Therefore, the balance equation, in the flame, is:

$$RI_{vacuum}^2 + h\pi d(T_g - T_c) = \epsilon\sigma\pi d(T_c^4 - T_0^4) \quad (2.11)$$

The lowest pressure used in this study is 0.64 mbar and not vacuum. However, the plot $I^2 = f(T)$ depends significantly on the pressure, see Figure 2.14. To

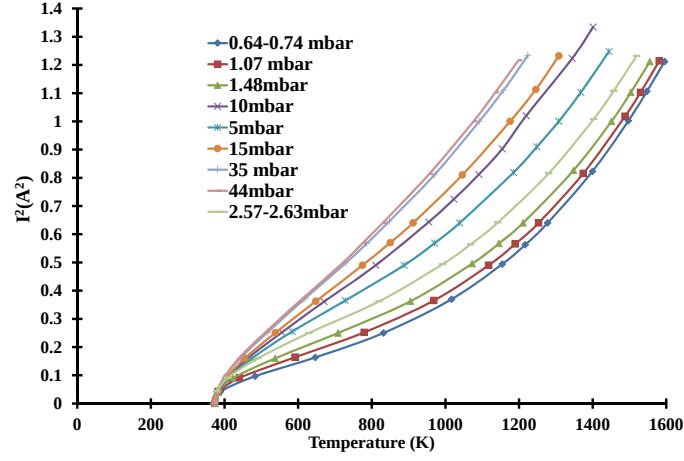


Figure 2.14: $I^2 = f(T)$ at different low pressure conditions in the combustion chamber.

estimate the data at perfect vacuum (0 mbar), we extrapolated the experimental values obtained at low pressure. Figure 2.15 shows the extrapolated curve. The obtained curve calculated from experimental data can be approximated

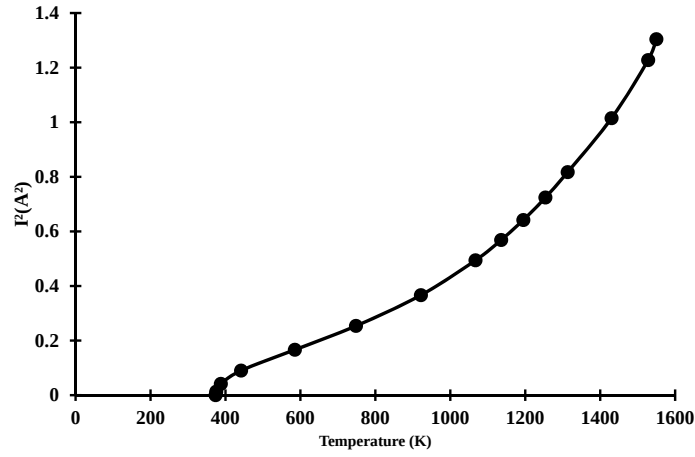


Figure 2.15: $I^2 = f(T)$ at 0 mbar calculated from experimental data.

by:

$$\begin{aligned}
 i^2 = & 98.423 + 0.699T_C + (-8.476 \times 10^{-4}T_C^2) \\
 & + (1.005 \times 10^{-6}T_C^3) + (-8.335 \times 10^{-10}T_C^4) \\
 & + (4.551 \times 10^{-13}T_C^5) \quad (2.12)
 \end{aligned}$$

At the intersection of the curves measured in vacuum and in the presence of the flame, the temperature is the same as well as the injected current (Figure 2.16). It means, that the thermocouple resistance is the same at this point. Then, we have:

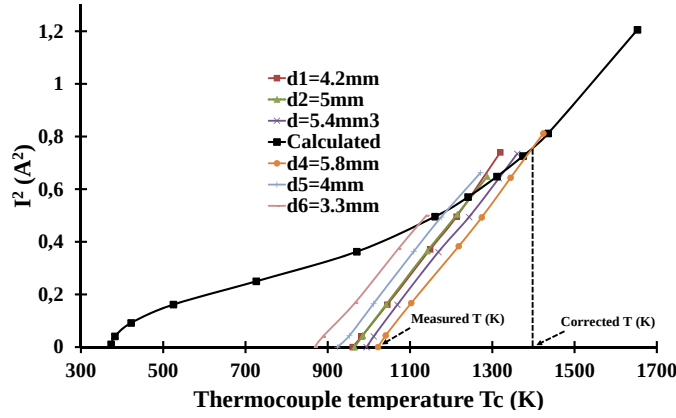


Figure 2.16: Evolution of $I^2=f(T)$ of the thermocouple temperature in vacuum (0 mbar) and at different distances from the burner in rich ethyl valerate flame.

$$(RI^2)_{flame} = (RI^2)_{vacuum} \quad (2.13)$$

From Equation 2.10, we can write that:

$$(RI^2)_{flame} = \epsilon\sigma\pi d(T_c^4 - T_0^4) \quad (2.14)$$

From Equation 2.11 using Equation 2.14, we obtain:

$$(RI^2)_{vacuum} + h\pi d(T_g - T_c) = (RI^2)_{flame} \quad (2.15)$$

From Equation 2.15, $T_g = T_c$ because $h\pi d(T_g - T_c) = 0$.

The correction can be calculated at different positions and at different temperatures.

In plotting the corrected temperatures as a function of the measured ones, the curve obtained is depicted in Figure 2.17 and the equation allows to correct the temperature profiles of the ethyl valerate flames studied. The type B thermo-

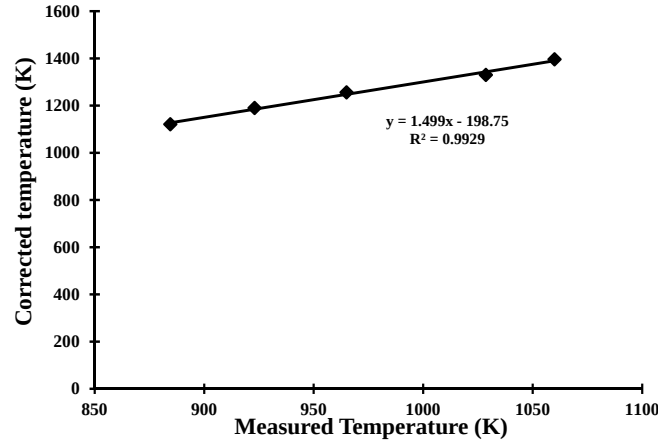


Figure 2.17: Evolution of the corrected temperature T_c as a function of the measured one T_g using a thermocouple B.

couple, used in this work, has a range of temperature measurements between 298.15 K and 2300 K. This thermocouple is very sensitive from 600 K. The total experimental uncertainty is estimated at 2.5% (approximately 50 K). In this total experimental uncertainty, 0.5% is the absolute uncertainty proposed by the manufacture and 2 % is the standard deviation calculated from the experimental data.

2.6.3 Temperature profiles

The minimum temperature observed is 516, 514 and 500 K for the lean, stoichiometric and rich flames, respectively (Figure 2.18). In the lean ethyl valerate flame, the maximum temperature is 1981 K at 17 mm. In the burned gases, the temperature decreases and reaches 1968 K. In the stoichiometric flame, the maximum temperature is 2193 K at 14 mm and in the burned gases the temperature is 2160 K. For the rich flame, its maximum temperature observed at 11 mm is 2243 K. This temperature decreases to 2162 K in the burned gases.

The measured temperature at the burner surface is 480, 542 and 578 K for the rich, stoichiometric and lean flame, respectively. These values depend on the

position of each flame from the burner.

The burner surface is mainly heated by radiations. The rich flame has a

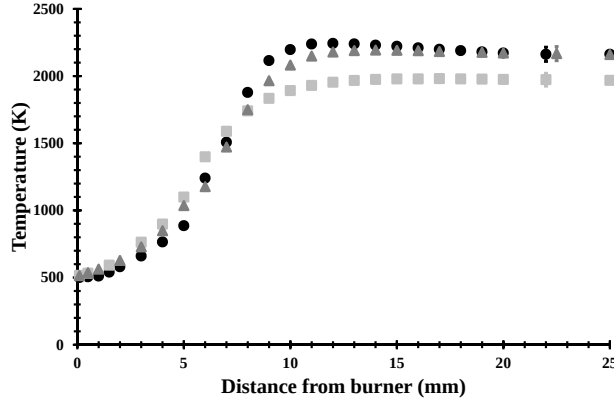


Figure 2.18: Experimental temperature profiles of the rich (black circles), stoichiometric (grey triangles) and lean (light gray squares) ethyl valerate flames.

higher emissivity, but a position far from the burner surface. The two effects compensate each other resulting in a lower temperature on the surface.

The high temperatures in the ethyl valerate flames are due to the low effective dilution by argon. The three temperature profiles are similar as the energy content of the mixtures are closed to each other.

Figure 2.19 shows the thermocouple in the combustion chamber with the rich ethyl valerate flame.

2.7 Ethyl valerate flame compositions

When a flame is stabilized at low pressure on the burner surface, the temperature and mole fraction profiles evolve with the distance from the burner. These parameters can be determined at each distance by moving, horizontally, the distance between the burner surface and the quartz nozzle.

The flame front is a zone where intermediate species are formed and consumed. This zone is also called "the reaction zone" where many intermediate species have high concentrations. Figure 2.20 represents an 1D stabilized flat flame with the different zones. The preheat zone is a part where fresh premixed gases (fuel, oxidizer and diluent) coexist. There is no reaction in this zone. The reaction zone is the front flame where intermediate species are formed and

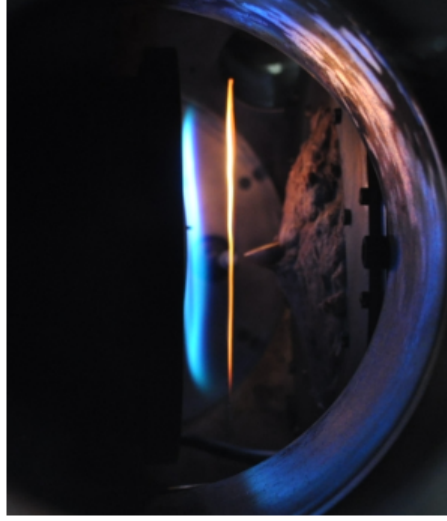


Figure 2.19: Picture of the combustion chamber with rich ethyl valerate flame (left), quartz nozzle (right) and thermocouple (middle).

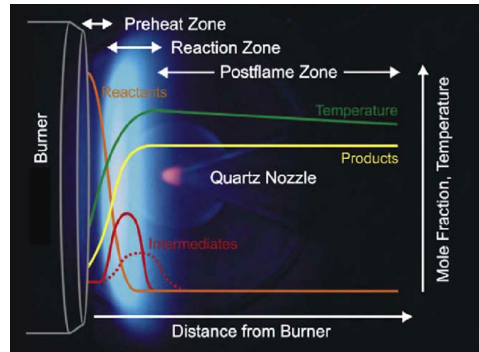


Figure 2.20: Example of one-dimensional laminar flat flame adapted from Hansen et al. [82].

consumed during combustion. The temperature increases in this zone. In the postflame zone, all chemical products of the combustion coexist such as H_2 , CO , CO_2 and H_2O . For stoichiometric and lean conditions, O_2 can remain in the post flame as a product. Depending on the equivalence ratio, some intermediate species can also be found in the postflame zone such as : C_2H_4 , C_2H_2 , CH_2O , etc, due to the incomplete combustion. In rich condition if the ratio C/O is higher than 0.7, soot are also formed. In this zone, the temperature increases and reaches a maximum value.

In this study, three flames have been stabilized on the burner at 55 *mbar*. To characterize the fuel combustion, three equivalence ratios (rich, stoichiometric and lean) must be studied to predict the combustion mode in these conditions. A complete detailed kinetic model must be able to predict with good fidelity the experimental data due to the effect of the equivalence ratio of the fuel. Practically, the three modes of combustion are used in the various industry applications (spark ignition engine: near stoichiometric condition, compression ignition engine: lean condition and rich condition locally; and furnaces). The flame compositions have been determined experimentally by trial and error. The objective was to obtain stable neat ethyl valerate flames. To achieve it, the fuel mass flow rate has been maximized and kept constant at 100 *g/h* for the three flames. The oxygen and argon mass flow rates have then been varied to obtain different equivalence ratios keeping a stable flame condition. To stabilize these flames, the pressure, the dilution and the total mass flow have been optimized. The most stable flame compositions are reported in Table 2.9. Figure 2.21 shows two pictures of the same rich ethyl valerate flat flame

Table 2.9: Inlet Compositions in mole fractions for three stabilized ethyl valerate flat flames at 55 *mbar*.

Φ	X_{EV}	X_{O_2}	X_{Ar}	Flow rate (<i>ln/min</i>)	Dilution (%)	<i>C/O</i>
1.31	0.039	0.282	0.679	7.36 ± 0.058	67.9	0.425
0.95	0.038	0.379	0.583	7.64 ± 0.060	58.3	0.319
0.81	0.037	0.435	0.527	7.67 ± 0.060	52.7	0.274

stabilized on the burner at 55 *mbar* but for two positions of the burner at 3 *mm* and 20 *mm* from the nozzle. The mixture ($C_7H_{14}O_2 - Ar - O_2$) is not



Figure 2.21: Picture of rich ethyl valerate flame at 20 *mm*(left) far from the quartz nozzle: burned gases and 3 *mm*(right) near the quartz nozzle: reaction zone.

highly flammable, so, we use ethylene to ignite the flame. After the ignition, ethylene is replaced by ethyl valerate by adjusting the flow rates of oxygen and argon and also the pressure in the combustion chamber, until the determined flame composition has been reached. The pressure in the combustion chamber for the ignition phase is 60 *mbar*.

The initial composition of the ethylene - oxygen and argon ($C_2H_4 - O_2 - Ar$) mixture used to ignite the flame is presented in appendix C.

The total mass fluxes are 0.0453, 0.0456 and 0.0449 $kg/m^2/s$ for the lean, stoichiometric and rich flames, respectively. The ratio C/O is lower than 0.7 for all the investigated flames. In these conditions, there is no soot formation during the combustion. As shown in Table 2.9, flames are diluted at 67.9, 58.3 and 52.7% with argon for the rich, stoichiometric and lean one, respectively. We do not use nitrogen to dilute the investigated flames to avoid NO_X formation during combustion. Argon is a neutral gas that cannot react with any species formed during the combustion.

2.8 ATEX directives

The experimental setup performed in this work is validated against the ATEX directives due to the utilization of flammable compounds. These ATEX directives are defined in the zones where explosive atmosphere could be created [83].

1. Zone 0 : areas in which explosive atmosphere consisting of a mixture with air and flammable substances in the form of gas, vapour or mist is present continuously for long periods or frequently.
2. Zone 1 : areas in which explosive atmosphere consisting of a mixture with air and flammable substances in the form of gas, vapour or mist is susceptible to run in normal operation occasionally.
3. Zone 2 : areas in which explosive atmosphere consisting of a mixture with air and flammable substances in the form of gas, vapour or mist is not susceptible to appear in normal operation or in short duration if this atmosphere is existing.

The startup procedures, the ATEX directives and the risk analysis of the experimental setup used in this work are presented in appendix CD.

Conclusion

The evaporation system used in this study allows to have good premixed condition between the fuel, the oxidizer and the diluent in order to study their combustion in a burner. To avoid condensation of the fuel, the experimental setup was adapted by including heat ribbons to avoid cold sections. Three ethyl valerate flames were stabilized and studied at low pressure. As the combustion is performed at 55 *mbar*, the sampling at 20 *mbar* and the GC is working at atmospheric pressure, a compression system is needed. This compression system allows to reach atmospheric pressure before each sample injection and is placed in-line between the combustion chamber and the gas chromatography. Three columns are used for GC analysis to separate and identify different chemical species formed during ethyl valerate combustion. The calibration of the GC allows to convert the TCD and FID intensity signals for each species into mole fractions. Two columns (CPSIL-5CB for hydrocarbons and oxygenated species and Molsieve for the permanent gases) were used to separate the sampling gases and the RTX-1 for flow rate obstruction before the microTCD. As the combustion is at 55 *mbar* and 20 *mbar* after the quartz nozzle, a compression system was used to increase the pressure of the sampled gas from low to atmospheric condition before its injection in the GC. To avoid condensation, heat ribbons were used at each cool part of all the experimental setup. Two detectors were used to identify different species formed during the ethyl valerate combustion. The analyzed chemical compounds are : $C_7H_{14}O_2$, O_2 , Ar, CO, CO_2 , H_2 , H_2O , C_4H_9COOH , CH_3CHO , CH_2O , CH_3COCH_3 , $OHCHO$, C_2H_4 , CH_4 and C_2H_2 . These stable chemical compounds were calibrated to allow conversion of their GC signal obtained with the *EzChrom* into mole fraction profiles. The experimental error is estimated at 5% for the main species such as O_2 , Ar, CO, CO_2 , and H_2O . It is 10% for H_2 and $C_7H_{14}O_2$ (EPE). For the other species, it is 20% for C_4H_9COOH , CH_3CHO , CH_2O , CH_3COCH_3 , $OHCHO$, C_2H_4 and CH_4 ; and 25% for C_2H_2 due to its low sensitivity to the used column. Three ethyl valerate flames have been stabilized on a burner at 55 *mbar*. The compositions of these flames have been adjusted by trial and error because of the difficulty to stabilize ethyl valerate flames. As the combustion is not adiabatic, experimental temperature profiles have been determined using a thin thermocouple. The radiation and the convection effects were taken into account by correcting the measured temperature profiles. The corrected temperature profiles presented in this study.

Finally, the experimental setup has been developed due to ATEX directives for ensuring the security, while working with flammable compounds.

Chapter 3

Numerical simulation

Introduction

During the combustion, a flame (chemical reacting flow) can be described at each point in term of space and time by specifying its physical properties such as the pressure, the temperature, the velocity and the density of each chemical species [84]. The fluid flow rate (molecular and energy convection, molecular diffusion, energy conduction and radiations) can change when chemical species are reacting.

To have a better comprehensive mathematical description of the flame, all these parameters have to be taken into account [84]. For fluid dynamics phenomena, Navier-Stokes equations can be used, these equations take non reacting flows into account. For other properties such as energy, mass and momentum conserved across the flame, the conservation reactions are described. To describe reacting flow such as flames, Poinot et al. [85] proposed some additional terms to the Navier-Stokes equations that can take into consideration multiple species and chemical reactions between them.

A detailed mathematical understanding of flame structures requires the utilization of conservation equations and a detailed kinetic model. A kinetic model enclosing the rates of each chemical species with its thermodynamic and transport properties, can be used in addition to describe the flame structure. The numerical study of flames requires, firstly, a complementary input from engineers in developing different tools, able to solve the complex conservation equations including fluid dynamic and physical properties of each involved species. Secondly, the use of kinetic model on these tools requires a supplementary ma-

terial from chemists.

Flames can be turbulent or laminar. In this work, the flame studied is laminar. In this chapter, the utilization of *Cosilab*® [12] software from Softpredict is described.

3.1 Cosilab software

Cosilab® software [12] from Rotexo GmbH & Co. is a combustion simulation software for different systems such as burners, reactors, engines, etc. In this section, this software is described for the case of one dimensional flat flame combustion. The complete functional *Cosilab*® scheme is presented in Figure 3.1. The mathematical aspect used to describe one-dimensional laminar flames is presented in Appendix A.

A chemical reacting flow such as a flame can be totally described in terms of space and time at each point by its physicochemical properties (pressure P , temperature T , velocity v and density ρ_i for each chemical species). In this work, the ethyl valerate flames are maintained at constant pressure during all experiments ($P = 55 \text{ mbar}$). The density ρ_i of each i species of the N chemical compounds constituting the flame is given by the product of its mass fraction w_i with the total density ρ . This means, that $N + 2$ variables are unknown: $(w_1, w_i, \dots, w_{N-1}, T, v \text{ and } \rho)$ because the remaining mass fraction w_N can be deduced using the balance: $\sum_i^N w_i = 1$.

Cosilab® software [12] from Rotexo GmbH & Co. uses the conservation equations to find these $N + 2$ unknown variables at each distance z from the burner. In addition, the kinetic model, thermodynamic and transport data of each involved species and the boundary conditions of the flame are considered to find these $N + 2$ variables. The experimental temperature profile is introduced to take into account the heat losses that are difficult to model. Indeed, the software could solve the energy equation but it would result to the adiabatic flame temperature. The other input parameters are the temperature at burner's surface and the total mass flux of reactants. Moreover, the molecular and thermal diffusions of species are taken into account.

Firstly, the software determines a system of equations based on all the input data and the conservation equations. Then, the Newton's method is used to solve this system of equations. The Newton's method is a process able to determine roots of a function by replacing the curve representing this function

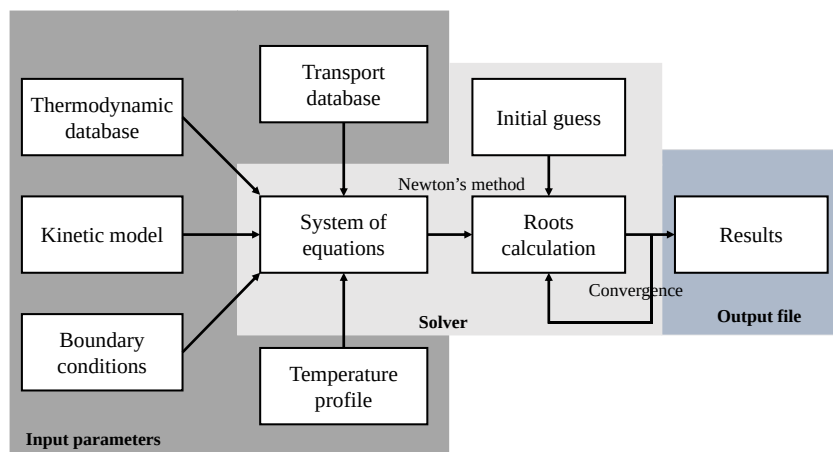


Figure 3.1: General resolution scheme of Cosilab® software.

by its tangent and then finding the intersection of the tangent with the x-axis if an initial guess is provided. The solver requires an existing initial solution sufficiently close to the final solution. This initial guess can be created from the initial composition of the flame by adding some concentrations of intermediate species and the products. The sum of the mole fractions of fresh gases (reactants) must be equal to the unity. The convergence level affects the computational time. Its adjustment is very important for improving the calculations. When the system of equations has converged using the Newton's method, an output file composed by the mole fractions of all the kinetic mechanism's species, the velocity and the temperature profile as a function of the space coordinate is provided in ".txt" or ".xls" form. An additional output file can be provided for the rate of chemical reactions used in the contribution calculations. This file is also a function of the coordinate of space z .

3.1.1 Input parameters

The input parameters are:

1. the boundary conditions
2. the experimental temperature profile
3. the kinetic model
4. the transport database

5. the thermodynamic database

Boundary conditions

The boundary conditions describe the burner surface conditions : the inlet composition of the fresh gases (fuel, oxidizer and diluent), the temperature at the surface of the burner T_s and the total mass flux ρv crossing this surface. The inlet compositions in mole fractions are presented in Table 2.9. The burner surface temperature is measured using a thermocouple placed at this surface. The values, in this work, are 480, 542 and 578 K for the rich, stoichiometric and lean flame, respectively.

The total mass flux ρv of the fresh gas mixture at the burner surface output is calculated using Equation (3.1).

$$\rho v = \sum_i Dv_i \frac{PM_i}{RT_s S_b} \quad (3.1)$$

where i represents each chemical compound of the fresh gases (fuel, oxidizer and diluent), M_i is a molecular mass of i ($[kg/mol]$), R is the ideal gas constant ($[0.082l.atm/mol.K]$), S_b is the burner surface ($[m^2]$) and Dv_i is the volumetric flow rate of i ($[l/min]$).

Experimental temperature profile

The experimental temperature profile is introduced into *Cosilab*®. The measurement of the temperature profile using a thermocouple is described in Chapter 2.

Thermodynamic database

Thermodynamic data of each species i are used in the determination of the rate constant of the reactions. The software calculates them by using a polynomial curve fit of NASA type [86]. These NASA coefficients consist in two sets of 7 coefficients ($a_1 - a_7$) and ($a_8 - a_{14}$), corresponding to high (1000 to 5000 K) and low (300 to 1000 K) temperature range, respectively. These 14 coefficients allow to calculate for each species i its molar heat capacity $c_{p,i}$, enthalpy h_i and entropy s_i at a given temperature, using the following Equations (3.2), (3.3) and (3.4):

$$c_{p,i} = R(a_1 + a_2 T + a_3 T^2 + a_4 T^3 + a_5 T^4) \quad (3.2)$$

$$h_i = R(a_6 + a_1T + \frac{a_2}{2}T^2 + \frac{a_3}{3}T^3 + \frac{a_4}{4}T^4 + \frac{a_5}{5}T^5) \quad (3.3)$$

$$s_i = R(a_7 + a_1\ln(T) + a_2T + \frac{a_3}{2}T^2 + \frac{a_4}{3}T^3 + \frac{a_5}{4}T^4) \quad (3.4)$$

Figure 3.2 shows an example of NASA coefficients of four species used in the present work. As illustrated in Figure 3.2, the first line gives the name of the

```

EPE      28/02/11  C   7H  140   20   0G   300.00   4000.00  1000.00      1
-0.18428167E+02  0.10309508E+00-0.45776756E-04  0.88162633E-08-0.62054685E-12  2
-0.55175238E+05  0.14531258E+03-0.38000696E+01  0.10646161E+00-0.80708494E-04  3
0.23426955E-07  0.14898342E-11-0.63917438E+05  0.52966770E+02      4
C4H9COOH 28/02/11  C   5H  100   20   0G   300.00   4000.00  1000.00      1
-0.69189329E+01  0.64535089E-01-0.27766657E-04  0.52291851E-08-0.36214152E-12  2
-0.56665328E+05  0.74433884E+02-0.92007560E+00  0.72700985E-01-0.53475036E-04  3
0.15775791E-07  0.52332227E-12-0.60991418E+05  0.33946636E+02      4
C4H9CO2  28/02/11  C   5H   90   20   0G   300.00   4000.00  1000.00      1
-0.42236457E+01  0.54956760E-01-0.21854379E-04  0.38934904E-08-0.25918281E-12  2
-0.30059875E+05  0.60040428E+02-0.10223966E+01  0.68892784E-01-0.50134327E-04  3
0.13308625E-07  0.14019566E-11-0.33488500E+05  0.34577267E+02      4
EPEMj    28/02/11  C   7H  130   20   0G   300.00   4000.00  1000.00      1
-0.14208113E+02  0.91219619E-01-0.38505012E-04  0.71539752E-08-0.49063802E-12  2
-0.31633492E+05  0.12500870E+03-0.46503553E+01  0.11535108E+00-0.10844434E-03  3
0.49842402E-07  0.70622926E-11-0.39301648E+05  0.57237679E+02      4

```

Figure 3.2: Example of NASA coefficients used in the present work.

chemical species (stable or radical), its elementary composition, the phase and the range of temperature used to calculate the properties. The elementary composition is used to determine the molar mass of the species in order to verify the good balance of the chemical reactions in the kinetic model. The three following lines represent the adopted NASA coefficients of the species in the two temperature domains, firstly at high temperature and secondly at low temperature. These coefficients can be determined using the Thergas software [87] based on the group additivity method proposed by Benson [88].

Transport database

The transport databases are used in the calculation of the coefficients D_{ij} , D_i^T and λ from Fick and Fourier laws. D_{ij} is the multicomponent diffusion coefficient, D_i^T is the thermal diffusion coefficient and λ represents the heat conductivity of the mixture. These coefficients are used in the determination of j_i (molecular diffusion) and j_q (heat conduction) parameters of the conservation equations for each species and the energy. These three parameters can be calculated for each species by providing into the transport database:

1. the geometry of the involved species (monatomic, linear, non linear)
2. the Lennard-Jones well depth ϵ
3. the Lennard-Jones collision diameter σ

4. the dipole moment δ
5. the polarizability α
6. the rotational relaxation collision number Z_{rot}

A comprehensive presentation of the relationships between these transport properties and the coefficients (D_{ij} , D_i^T and λ) can be found in a paper from Kee et al. [89].

Figure 3.3 illustrates an example of transport data used in this study:

The thermal diffusion effect taken into account is the "Soret effect". *Cosi-*

	Species	Geometry	L.J. Potential	L.J. Coll. Diameter	Dipole Moment	Polarizability	z Rotation
2	Ar	monatomic	1.365000e+002	3.330000e+000	0.000000e+000	0.000000e+000	0.000000e+000
3	As	monatomic	1.045500e+003	4.580000e+000	0.000000e+000	0.000000e+000	0.000000e+000
4	AsH	linear	1.993000e+002	4.215000e+000	0.000000e+000	0.000000e+000	1.000000e+000
5	AsH2	nonlinear	2.296000e+002	4.180000e+000	0.000000e+000	0.000000e+000	1.000000e+000
6	C	monatomic	7.140000e+001	3.298000e+000	0.000000e+000	0.000000e+000	0.000000e+000
7	C2	linear	9.753000e+001	3.621000e+000	0.000000e+000	1.760000e+000	4.000000e+000
8	C2O	linear	2.324000e+002	3.828000e+000	0.000000e+000	0.000000e+000	1.000000e+000
9	CN2	linear	2.324000e+002	3.828000e+000	0.000000e+000	0.000000e+000	1.000000e+000
10	C2H	linear	2.653000e+002	3.721000e+000	0.000000e+000	0.000000e+000	2.500000e+000
11	C2H2	linear	2.653000e+002	3.721000e+000	0.000000e+000	0.000000e+000	2.500000e+000
12	C2H2OH	nonlinear	2.247000e+002	4.162000e+000	0.000000e+000	0.000000e+000	1.000000e+000
13	C2H3	nonlinear	2.653000e+002	3.721000e+000	0.000000e+000	0.000000e+000	1.000000e+000
14	C2H4	nonlinear	2.384000e+002	3.496000e+000	0.000000e+000	0.000000e+000	1.500000e+000

Figure 3.3: Examples of transport data used in the present work.

lab® [12] solves this effect by considering the species mass diffusion due to a temperature gradient. This phenomenon is more pronounced for light species such as H_2 that diffuses rapidly in the flame due to the temperature gradients.

Kinetic model

The mechanism contains the kinetic parameters of chemical reactions involved in the studied flame. Indeed, a combustion is a complex process including a large number of species linked by reversible and/or none-reversible chemical reactions. Their number depends on the chemical structure of the studied fuel and the desired degree of accuracy. The developed kinetic mechanisms are tested and validated by comparison with the experimental data in different setup of combustion such as reactors, burners, shock tubes, etc., at different equivalence ratios (rich, stoichiometric and lean) and conditions of pressure and temperature. The validated kinetic mechanisms are able to simulate the formation and consumption of many chemical compounds such as pollutants. The detailed models containing numerous chemical reactions and chemical species, can be reduced to be included in the calculation of engineering processes with

complex fluid dynamic behaviours (engines, furnaces, ...).

For simulation, the input file for the kinetic model has two main sections. The first section lists all chemical species (fuel, oxidizer, intermediate species and products) involved in the mechanism. The second part gives elementary chemical reactions with their kinetic parameters. These kinetic coefficients are the pre-exponential factor (A), the temperature exponent (n) and the activation energy (E_a). These parameters allow to calculate with the modified Arrhenius's law, the rate constant value (k) of the reaction as a function of the temperature:

$$k = AT^n \exp\left(\frac{-E_a}{RT}\right) \quad (3.5)$$

In Equation (3.5), R is the ideal gas constant in [$l.atm/mol.K$], E_a in [cal/mol] and T in [$Kelvin$].

The elementary reactions can be reversible ("=") or not reversible ("→") .

Figure 3.4 illustrates the kinetic mechanism used in the present work.

```

!Haddy.MBUYI KATSHIATSHIA
ELEMENTS
  H C O N Ar
END
SPECIES
CO O2 CO2 H2O CH4 H2 C2H2 C4H9COOH EPE C2H4
CH2O CH3CHO C2H5CHO NC3H7CHO C2H3COOH C2H3CHO
C3H6 C4H8-1 CH3OH C4H6 C2H6 EA EP
CH3COOH C2H5COOH C3H8 NC4H10 C3H4-A C3H4-P
C2H5OH H2O2 CH3COCH3
CH2CO C2H4O1,2 C4H4 C3H7COOH
END

REACTIONS CAL/MOLE
!!-----
EPE = C4H9COOH+C2H4 2.000000E+012 0.000000E+000 4.729000E+004
EPE5j+H(+M) = EPE(+M) 1.000000E+014 0.000000E+000 0.000000E+000
  LOW /9.742000E+103 -2.461000E+001 1.153800E+005/
  TROE /8.720000E-001 9.990000E+009 2.926400E+001 7.596100E+007/
EPE+H = EPE5j+H2 9.400000E+004 2.750000E+000 6.280000E+003 !2 ANC7, Primary F
EPE+H = EPE4j+H2 1.300000E+006 2.400000E+000 4.471000E+003 !2 ANC7, Secondary
EPE+H = EPE3j+H2 1.300000E+006 2.400000E+000 4.471000E+003 !2 ANC7, Secondary
EPE+H = EPE2j+H2 1.300000E+006 2.400000E+000 4.471000E+003 !2 ANC7, Secondary
EPE+H = EPEEj+H2 1.794000E+005 2.530000E+000 3.420000E+003 !
EPE+H = EPEMj+H2 9.400000E+004 2.750000E+000 6.280000E+003 !2 ANC7, Primary F
EPE+O = EPE5j+OH 9.650000E+004 2.680000E+000 3.716000E+003 !2 ANC7, Primary F
EPE+O = EPE4j+OH 4.770000E+004 2.710000E+000 2.106000E+003 !2 ANC7, Secondary
EPE+O = EPE3j+OH 4.770000E+004 2.710000E+000 2.106000E+003 !2 ANC7, Secondary
EPE+O = EPE2j+OH 4.770000E+004 2.710000E+000 2.106000E+003 !2 ANC7, Secondary
EPE+O = EPEEj+OH 1.450000E+005 2.410000E+000 8.760000E+002 !
EPE+O = EPEMj+OH 9.650000E+004 2.680000E+000 3.716000E+003 !2 ANC7, Primary F
EPE+OH = EPE5j+H2O 5.250000E+009 9.700000E-001 1.590000E+003 !2 rNC7, Primary;
EPE+OH = EPE4j+H2O 4.680000E+007 1.610000E+000 -3.500000E+001 !2 rNC7, Secondary
H+O+M = OH+M 4.714000E+018 -1.000000E+000 0.000000E+000 !Keromnes (2013)
  H2O /1.200000E+001/ H2 /2.500000E+000/ CO /1.500000E+000/ CO2 /2.000000E+000/
END

```

Figure 3.4: Example of kinetic mechanism used in the present work.

Reversible reactions

The general form of an elementary reversible reaction is presented by the following chemical reaction: $A + B \xrightleftharpoons[k_b]{k_f} C + D$

The kinetic parameters are only used to determine the forward rate constant of the reaction k_f . The backward rate constant of the same reaction can be calculated at each given temperature T by Equation (3.6).

$$\frac{k_f}{k_b} = K_{p(T)} = e^{\left(\frac{-\Delta H + T\Delta S}{RT}\right)} \quad (3.6)$$

In Equation (3.6), $K_{p(T)}$ is the gas equilibrium constant, expressed in terms of partial pressures P_i as depicted in Equation (3.7).

$$K_{p(T)} = \frac{P_C \cdot P_D}{P_A \cdot P_B} \quad (3.7)$$

To compute partial pressure of each species i , the software could use Equation (3.8), in-which R , T , ρ_i and M_i are the ideal gas constant, the temperature, its density and its molecular mass, respectively.

$$P_i = \frac{\rho_i}{M_i} \times RT \quad (3.8)$$

The forward rate constant k_f calculated from the Arrhenius Equation (3.5), represents the consumption rate of A and B to produce C and D . As demonstrated before, the backward rate constant k_b can be calculated from Equation (3.6). In this case, the thermodynamic data (h_i and s_i) of each i species are used at temperature T . Equations (3.9) and (3.10) allow to calculate the variation of enthalpy and entropy involved in an elementary reaction. The chemical reaction must be an elementary reaction: the reactants react simultaneously at a same point to form the products without intermediate species. In fact, all reactions in the kinetic mechanisms are elementary reactions to ensure this property.

$$\Delta H = (h_C + h_D) - (h_A + h_B) \quad (3.9)$$

$$\Delta S = (s_C + s_D) - (s_A + s_B) \quad (3.10)$$

The net rate formation of a species i , involved in an elementary reversible reaction can be calculated by subtracting its consumption rate to its formation

one:

$$\forall i \in \text{reactants} \frac{d[i]}{dt} = k_b \times \prod_{i=\text{products}} [i] - k_f \times \prod_{i=\text{reactants}} [i] \quad (3.11)$$

$$\forall i \in \text{products} \frac{d[i]}{dt} = k_f \times \prod_{i=\text{reactants}} [i] - k_b \times \prod_{i=\text{products}} [i] \quad (3.12)$$

None reversible reactions

A none reversible elementary reaction as presented in Equation (3.13) is written in the kinetic model by replacing " = " with " $\rightarrow$ ". As shown in the present equation, this reaction has only one rate constant for the consumption of reactants into products, k_f .



The reverse rate constant is not taken into account in the calculation. Thus, the net rate of formation of species i can therefore be calculated using Equations (3.14) and (3.15).

$$\forall i \in \text{reactants} \frac{d[i]}{dt} = -k_f \times \prod_{i=\text{reactants}} [i] \quad (3.14)$$

$$\forall i \in \text{products} \frac{d[i]}{dt} = k_f \times \prod_{i=\text{reactants}} [i] \quad (3.15)$$

Pressure dependent reactions

Some rate constants depend on the pressure. It is the case for recombination reactions in which two reactants form one product, and for dissociation reactions : $A + M \xrightleftharpoons[k_b]{k_f} B + C + M$.

The pressure dependence is taken into account by inserting a third body M in the reaction as shown above. This third body M of the gas phase does not have the same collision efficiency. It represents all the other molecules of the system. From the chemical point of view, this third body is neutral. Its presence only shows that the rate constant is influenced by the presence of others molecules in term of concentration i.e. partial pressure. The chemical rate constant is

defined by the Lindemann-Hinshelwood's Equation (3.16) [90, 91].

$$k = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty} \quad (3.16)$$

The kinetic parameters for these reactions, are the rate constant values when the pressure P tends to 0 (k_0) and to ∞ (k_∞). Therefore, the influence of the pressure appears in terms of concentration of the third body ($[M]$) calculated by the ideal gas law (Equation (3.17)):

$$[M] = \frac{n}{V} = \frac{P}{RT} \quad (3.17)$$

Troe [92, 93] and Gilbert et al. [94] demonstrated, that the Lindemann-Hinshelwood Equation (3.16) are not able to take into account the *Fall off curve*. This zone corresponds to the intermediate pressures between the high ($k \approx k_\infty$) and low ($k \approx k_0$) pressure systems. To solve this problem, they proposed to multiply the Lindemann-Hinshelwood Equation (3.16) by a factor F .

This factor is calculated using empirical equations proposed by Troe [92, 93] including four parameters (a , T^* , T^{**} and T^{***}) called "Troe parameters". The rate constant depending on the pressure is calculated using these following Equations (3.18), (3.19) and (3.20).

$$k = \frac{k_0 k_\infty [M]}{k_0 [M] + k_\infty} F \quad (3.18)$$

with

$$\text{Log} F = \frac{\log F_c}{1 + \left[\frac{\log(k_0 [M] / k_\infty)}{0.75 - 1.27 \log F_c} \right]^2} \quad (3.19)$$

and

$$F_c = (1 - a) \exp\left(-\frac{T}{T^{***}}\right) + a \exp\left(-\frac{T}{T^*}\right) + \exp\left(-\frac{T^{**}}{T}\right) \quad (3.20)$$

The third body efficiency depends also on its chemical structure. Kinetic models take into account this effect by including coefficients called "third body efficiency". Each chemical species has its own coefficient. If this coefficient is omitted, its value is set to 1, automatically. These values are also written in the kinetic model with their specifications for the reactions containing the third body represented by "(M)" (Figure 3.4).

3.1.2 System of equations

Due to the input parameters (thermodynamic database, transport database, the kinetic model, boundary conditions and temperature profile), the software is able to write the system of equations in order to solve them by using Newton's method as related in Section 3.3.

These equations are:

1. one linear equation (perfect gas law)
2. N differential equations (momentum + species conservation)
3. one constraint stipulating that the sum of species mass fraction is 1

Equation of state

The first equation is linear and allows to calculate the total density of the mixture, ρ . This parameter is calculated at temperature T using the ideal gas law as depicted in Equation (3.21):

$$\rho = \frac{m}{V} = P \frac{\sum_i^N w_i M_i}{RT} \quad (3.21)$$

M_i is the molecular mass of each chemical compound, that means $\sum_i w_i M_i$ is the average molecular mass of the mixture.

Equation of the total mass conservation

The equation of the total mass conservation is the first differential equation. It is described in Appendix A in Equation (A.8) then extended in Equation 3.1 : the product ρv is constant all along the flame. The velocity v of the flow can be calculated at any distance z of the burner if the total density ρ is known.

Equation of species conservation

The conservation equations for species are the second differential equations as depicted in Appendix A in Equation (A.12). In this equation, the unknown parameters are ρ , v , w_i and T . r_i can be calculated with the kinetic model. The molecular diffusion " j_i " from Equation (A.19) may be calculated from thermodynamic and transport database in addition with Equation of state (3.21). Moreover, the sum of N mass fraction w_i is equal to unity (Equation

(3.22)). The temperature is given via the experimental temperature profile.

$$\sum_i^N w_i = 1 \quad (3.22)$$

Equation of energy conservation

The last differential equation is the energy conservation equation (see Equation (A.17)). In this equation, the unknown parameters are the same as for the equation of species conservation. $c_{p,i}$, h_i , r_i are the terms involved in j_i and j_q (Equations (A.19) and (A.20)). It should be noted that, in our case, Cosilab® does not solve this equation due to an existing temperature profile.

3.1.3 The output file

Once the solution has converged, the software writes an output file containing for n distances from the burner (z -axis), the calculated $N + 2$ variables (w_i , w_{i+1} , w_{n-1} , T , v and ρ). This file can easily be imported in *Excel*® for further analysis. Instead of terms of mass fraction, the output file can be expressed in mole fractions of each species, using this conversion Equation (3.23):

$$w_i = \frac{M_i}{M} x_i \quad (3.23)$$

Where w_i , M_i , M and x_i are the mass fraction of species i , the molecular mass of species i , the molecular mass of the mixture and the mole fraction of species i , respectively.

3.1.4 Contribution calculation

The analysis of the formation and consumption pathways of each species i is important. This analysis allows to compare the simulated net rate of formation and consumption of each species. The contribution calculations are used to analyze the fuel pathway consumptions, and the implication of each species during combustion.

Ancia [95] developed an *Excel*® macro that determines the net velocity of formation and consumption of each species at all the distances from the burner. The macro looks for all chemical reactions in which the i species is involved. Then a separated spreadsheet containing all the net reaction rate profiles involving i is generated. To assess the relative weight of a reaction j forming

or consuming i , the tool compares the surface S_j delimited by its curve of net reaction rate to the sum of those involved in formation or consumption of i , respectively.

The surface S_j is delimited by the z -axis and the curve of the net reaction rate involving j , by summing surfaces A_n of every rectangle n centred on a coordinate z_n , as depicted in Figure 3.5 and Equation (3.24). The grid used by the software is about 200 points, homogeneously distributed along the 2 cm of the considered reaction zone. The distance $z_n - z_{n-1} = z_{n+1} - z_n$ is approximately about 0.017 and Equation (3.24) represents a good approximation of S_j .

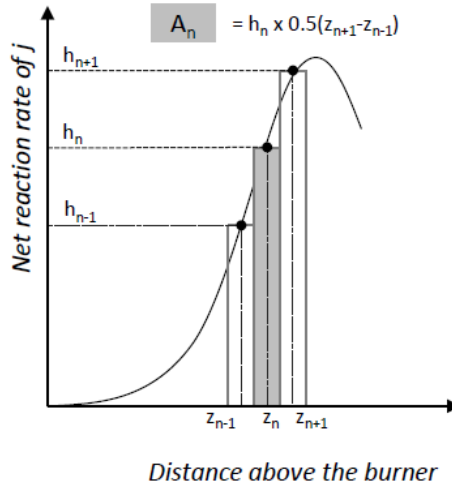


Figure 3.5: Calculation of the surface S_j under the curve of net reaction rates.

$$S_j = \sum_n A_n = \sum_n h_n \times 0.5(z_{n+1} - z_{n-1}) \quad (3.24)$$

Then the contribution C_j of each chemical reaction j involving the species i is calculated by dividing the absolute surface S_j by the sum of all absolute surfaces S_j according to Equation (3.25):

$$C_j = \frac{|S_j|}{\sum_j |S_j|} \quad (3.25)$$

The contribution can either be calculated for the formation or for the consumption of each species followed Equation (3.25). The values of C_{fj} and C_{cj} are the contribution of the formation of i species and the contribution of its

consumption, respectively. These values allow to determine the main reaction channels for the formation and the consumption of species i .

Conclusion

In this chapter, the mathematical description of the flame structure has been presented as implemented in the *Cosilab*® software. These mathematical concepts have been used to describe an one-dimensional premixed laminar flat flame stabilized on a burner. The conservation equations of the mass, species and the energy has been used to show how the software can solve these equations to determine flame structures. The input parameters such as temperature profile, boundary conditions, thermodynamic database, transport database and kinetic model have also been described. Finally, the calculation of the net rate constant of reactions determining the contribution of each species in the kinetic model, has been presented.

Chapter 4

Results and discussion

Introduction

The results obtained from the experiments are presented and discussed in this Chapter. Firstly, the bond dissociation energies of ethyl valerate are calculated using *ab initio* methods to show different ruptures in this molecule at 0 and 298.15 *K*. Taking into account the bond dissociation energies, a new detailed kinetic model is elaborated from two previous mechanisms (Dayma and UCL). Secondly, The elemental balance is used in this chapter to check the total combustion balance. The experimental mole fractions of the input and the output species are used to calculate the elemental balance of carbon, hydrogen and oxygen atoms in comparison with the simulated ones including the radicals H, OH and O. Thirdly, the mole fraction profiles of all the analyzed species are discussed in comparison with the simulated ones obtaining from the new detailed kinetic model named: "Katshiatshia mechanism". From the simulated results, ethyl valerate consumption pathways are elaborated for the three studied equivalence ratios. A synthetic common ethyl valerate consumption pathways is then presented. Fourthly, the predictions using the new mechanism are also compared to the Dayma's results obtained for the ethyl valerate oxidation at 10 *atm* in a jet-stirred reactor. Fifthly, the kinetic model elaborated in this work, is tested at high pressure, in a jet-stirred reactor at stoichiometric condition, to extend its reliability. Then, the mechanism is also tested against the laminar burning velocities experimental data from Lund University for extending its validity at atmospheric pressure. Four elementary reactions are assumed to be sensitive with the pressure, their modification leads to modifications in

the Katshiatshia mechanism. Finally, Katshiatshia and Katshiatshia modified mechanisms are compared with the experimental data performed in the present work.

4.1 Ethyl valerate kinetic model

4.1.1 Bond dissociation energies

To develop a kinetic model of ethyl valerate (ethyl pentanoate: EPE), theoretical calculations have been performed to estimate the different bond dissociation energies (BDE) with the help of Jules Tshishimbi Muya. The BDE of ethyl valerate chemical structure were computed using the Unrestricted Couple Cluster theory with Single and Double excitations (UCCSD) at 6-31G(d,p) and 6-31G(d) theoretical levels [96, 97]. The results present larger values of 5 *kcal/mol* to those reported by Nahas et al. for a similar molecule (ethyl propanoate) [98]. Indeed, these methods use many estimations in their calculations and the results are not accurate compared to the experimental ones or to those obtained using higher quality basis sets. To improve the accuracy of these results, qualitatively, high ab initio calculation methods namely G3B3, CBS-QB3, G4 and G4MP2 have been used at 0 *K* and at 298.15 *K*. Gaussian-n (Gn) methods are composite quantum mechanic methods divided in fourth levels, G1, G2, G3 and G4. These methods differ by the optimization calculations and the basis sets used [99]. In the present thesis, we report the results obtained with G3B3 and G4, the more accurate composite methods in the Gn series, compared to the UCCSD calculations at absolute temperature (0 *K*).

In the G3 theory, a sequence of well-defined ab initio molecular orbital calculations is performed to obtain the total energy of the molecular species. The geometries are optimized by using the second-order Moller-Plesset perturbation theory (MP2) for G3 or B3LYP density functional theory (DFT) for G3B3. Then, the correlation level calculations are done with MP4 perturbation theory and with quadratic configuration interaction [100, 101, 102].

The Gn methods are not used for molecular species with strongly correlated molecular systems such as diradicals (e.g. methylene, CH₂) and for systems composed with transition methods and degenerated molecular orbitals. Diradicals are species with a pair of degenerate molecular orbitals (equal energy) and two electrons.

G4 theory is similar to G3 theory. In this case, the geometries are optimized using B3LYP density functional theory (DFT) with large basis set. The correlation level calculations are performed using MP4 perturbation theory and the coupled cluster theory. For G4MP2, the optimization is performed with MP2 [103]. The difference between the experimental and the calculated data is between 0.2 and 1 *kcal/mol* for these methods.

The Complete basis set-QB3 (CBS-QB3) is also compared in the computation of BDE of ethyl valerate with Gn and UCCSD methods. The results with CBS-QB3 are very similar to G3B3 results, and those for G4 are similar to G4MP2 results.

The CBS-QB3 starts with a geometry optimization at B3LYP level as in G4 method, followed by a frequency calculation to obtain thermal corrections, zero-point vibrational energy and entropic information. In these calculations, the next three computations are single-point calculations at the CCSD(T) (Couple Cluster theory with Single and Double excitations attempt to treat the effects of Triply excited determinants upon both single and double excitation operators), MP4SDQ (fourth-order Moller-Plesset perturbation theory with Single, Double and Quadruple substitutions) and MP2 levels [99]. The results carried out with these calculations are very closed to the experimental ones with an absolute deviation of 1.1 *kcal/mol* [104].

The methods with high accuracy such as G4MP2, G4 and G3B3 take more time in calculations and produce results with less uncertainties compared to the experimental ones, than those with less accuracy such as UCCSD.

The chemical structure of ethyl valerate is presented in Figure 4.1.

The total atomization energy (TAE) at 0 *K*, the enthalpy of formation, the

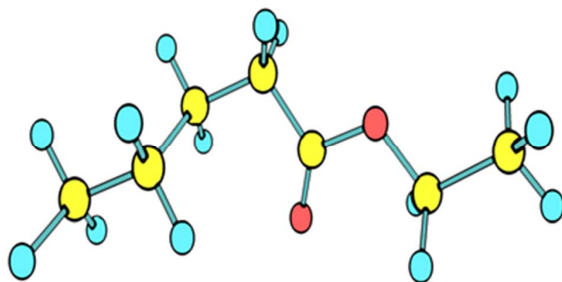


Figure 4.1: Chemical structure of ethyl valerate: grey (carbon atom), black (oxygen atom), dark grey(hydrogen atom).

free energy of formation and the entropy of formation of ethyl valerate at 298.15

K computed using G3B3 and G4 methods are depicted in Table 4.1. Table 4.2

Table 4.1: Total atomization energy, enthalpy, free energy and entropy of formation of ethyl valerate computed using G3B3 and G4.

$C_7H_{14}O_2$	G3B3 method	G4 method
TAE in eV	102.13	102.14
$\Delta H_{formation}$ in kcal/mol	-324.73	-322.58
$\Delta G_{formation}$ in kcal/mol	-150.60	-148.31
$\Delta S_{formation}$ in cal/mol	-584.03	-584.50

presents the results of the ethyl valerate BDE computed with UCCSD, G3B3 and G4 methods at 0 K. The results obtained with these calculations can pre-

Table 4.2: Bond dissociation energies of ethyl valerate computed at 0 K in [kcal/mol].

Bonds	UCCSD/6-31G(p)	UCCSD/6-31G(d,p)	G3B3	G4
$C_1 - H$	107.43	106.99	102.14	99.86
$C_2 - H$	102.49	101.79	-	94.74
$C_3 - H$	98.22	97.21	93.48	91.27
$C_4 - H$	103.78	103.32	98.87	96.41
$C_5 - H$	103.18	102.70	97.89	95.64
$C_6 - H$	105.87	105.52	100.36	98.06
$C - C_1$	96.38	94.38	88.16	85.94
$C - C_2$	94.84	92.84	89.03	87.13
$C - C_3$	102.42	100.30	100.14	97.17
$C - C_4$	98.04	95.30	93.36	90.56
$C - C_5$	91.61	89.31	85.37	83.33
$C - C_6$	94.07	92.29	89.03	85.01
$C - C_7$	-	93.22	88.16	85.12

dict the weakest bond in ethyl valerate thermal decomposition. The molecular enthalpy at 298.15 K of ethyl valerate chemical structure is -424.42 kcal/mol. At absolute temperature (0 K), the energy calculated is only the electronic energy. The other energies are null due to their dependency to T .

To take into account the other forms of energy (rotational, vibrational, transitional, etc.) in the determination of BDE, additional calculations were done at

298.15 K using G3B3, CBS-QB3, G4 and G4MP2 methods. The BDE values of ethyl valerate computed at 298.15 K are summarized in Table 4.3.

Table 4.3: Bond dissociation energies of ethyl valerate computed at 298.15 K in [kcal/mol].

Bonds	CBS-QB3	G3B3	G4	G4MP2
$C_1 - H$	103.27	102.07	100.97	99.92
$C_2 - H$	98.10	97.50	96.24	95.13
$C_3 - H$	94.14	93.66	92.62	91.65
$C_4 - H$	100.04	99.23	97.96	97.00
$C_5 - H$	99.04	98.38	97.26	96.29
$C_6 - H$	101.82	100.77	99.64	98.57
$C - C_1$	91.32	89.94	87.76	86.68
$C - C_2$	91.07	90.22	88.33	87.17
$C - C_3$	101.50	100.79	97.84	96.07
$C - C_4$	94.44	95.22	91.65	90.16
$C - C_5$	87.42	86.52	84.48	83.52
$C - C_6$	89.93	88.80	86.70	90.58
$C - C_7$	90.58	89.05	87.09	86.21

Figure 4.2 shows the different bond dissociation energies in kcal/mol calculated for this molecule with the G4MP2 method. Considering the different

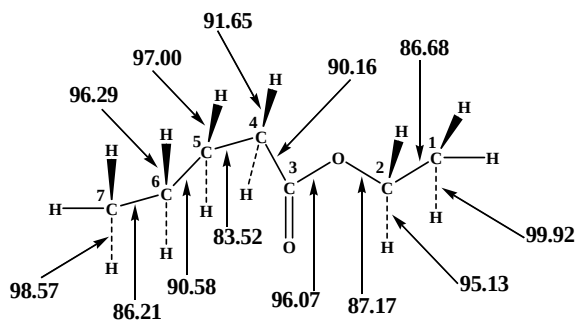


Figure 4.2: Bond dissociation energies of the ethyl valerate molecule [kcal/mol] computed with the G4MP2 method.

BDE values presented in Tables 4.2 and 4.3, at both temperatures, the order of bond dissociation energies appears to be the same in all investigated meth-

ods. However, the values show some discrepancies due to the sensibility of the method and the basis sets used. G4 and G4MP2 present the lowest values with an absolute deviation of 0.74 kcal/mol in average. In this thesis, only the values obtained using G4MP2 method will be discussed.

The first dissociation of the ethyl valerate molecule can be predicted by the BDE values. The weakest bond has the smallest value of BDE, this bond is expected to be the first broken during the thermal decomposition. The smallest BDE is estimated to 83.52 kcal/mol . The respective radical species expected to be produced from ethyl valerate are: $\text{CH}_3\text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{COOCH}_2\text{CH}_3$. The other radicals (C – C ruptures and C – O rupture) stemming from low BDE values are:

1. CH_3 and $\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$: 86.21 kcal/mol
2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2$ and CH_3 : 86.68 kcal/mol
3. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COO}$ and CH_3CH_2 : 87.17 kcal/mol
4. $\text{CH}_3\text{CH}_2\text{CH}_2$ and $\text{CH}_2\text{COOCH}_2\text{CH}_3$: 90.16 kcal/mol
5. CH_3CH_2 and $\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$: 90.58 kcal/mol
6. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{CO}$ and OCH_2CH_3 : 96.07 kcal/mol

The first decomposition of ethyl valerate produces β -scission radicals. The ruptures between the C-C bonds are more promoted than the ruptures between the C-H bonds due to the BDE values.

The C-H bond fissions in ethyl valerate molecule produce the following radicals:

1. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCOOCH}_2\text{CH}_3$ (EPE_{2j}) and H : 91.65 kcal/mol
2. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCHCH}_3$ (EPEM_j) and H : 95.13 kcal/mol
3. $\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$ (EPE_{4j}) and H : 96.29 kcal/mol
4. $\text{CH}_3\text{CH}_2\text{CHCH}_2\text{COOCH}_2\text{CH}_3$ (EPE_{3j}) and H : 97.00 kcal/mol
5. $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$ (EPE_{5j}) and H : 98.57 kcal/mol
6. $\text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_2\text{COOCH}_2\text{CH}_2$ (EPEE_j) and H : 99.92 kcal/mol

All these decompositions have been introduced by Dayma et al. [11] in the mechanism for ethyl valerate combustion at high pressure.

The discussion of these dissociations and their impact on the ethyl valerate

mechanism developed in this study will be presented in the section about the ethyl valerate simulated consumption pathways (Section 4.4).

4.1.2 Ethyl valerate kinetic model

In this section, we present the ethyl valerate detailed kinetic model elaborated from Dayma [11] and UCL mechanisms [65].

The first study on ethyl valerate combustion has been performed by Dayma et al. [11]. They studied experimentally and numerically the oxidation of ethyl valerate in a jet-stirred reactor (JSR) and the laminar burning velocities in a spherical combustion chamber. Firstly the authors investigated at 10 *atm* the ethyl valerate combustion in a jet-stirred reactor (JSR) at different equivalence ratios ($\phi = 0.6, 1$ and 2) and temperatures (550, 650, 750, 850, 950, 1050 and 1150 *K*). From these experimental data, they elaborated a detailed kinetic model. The simulated results are in good agreement with the experimental mole fractions of the measured species. The following species have been measured: ethyl valerate, O_2 , CO , CO_2 , H_2O , CH_2O , CH_4 , C_2H_2 , C_2H_4 , C_2H_6 , C_3H_6 , C_4H_8-1 , CH_3CHO , $1,3-C_4H_6$, 2-propenal, propanal, butanal and ethyl propenoate. The authors reported that the experimental error for the valeric acid measurements were too important to be taken into account in the kinetic model validation.

From these data, the authors elaborated a detailed kinetic model able to reproduce with good agreement the oxidation of ethyl valerate at high pressure at different equivalence ratios ($\phi = 0.6, 1$ and 2). This kinetic model named, in this work, "Dayma mechanism" contains 2719 elementary reactions and 522 chemical species.

They elaborated an ethyl valerate consumption pathways at $\phi = 1$, 10 *atm*, at 620 *K* (Figure 4.3) and 830 *K* (Figure 4.4). At 620 *K*, the ethyl valerate consumption produces large oxygenated compounds (more than 2 atoms of oxygen) before its decomposition in small chemical species (Figure 4.3). At this low temperature, the main consumption of ethyl valerate does not lead to the formation of β -scission products.

At 830 *K*, the first decomposition of ethyl valerate produces stable molecules such as ethylene (C_2H_4) and valeric acid (C_4H_9COOH) with a contribution of 32%, and 63% for the radical EPEXj. The EPEXj represents the six primary radicals obtained by H-abstraction from ethyl valerate and are: EPE_2j , EPE_3j , EPE_4j , EPE_5j , $EPEEj$ and $EPEMj$. At this temperature, the six primary rad-

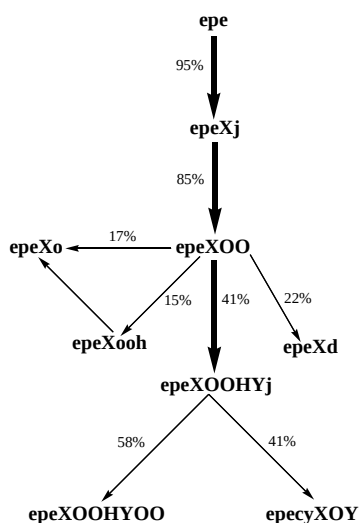


Figure 4.3: Reaction pathways from the kinetic modelling of ethyl valerate oxidation in a JSR at $\phi = 1$, $P = 10$ atm at 620 K [11].

icals lead the formation of β -scissions products.

Secondly, the same authors studied the laminar burning velocities of ethyl

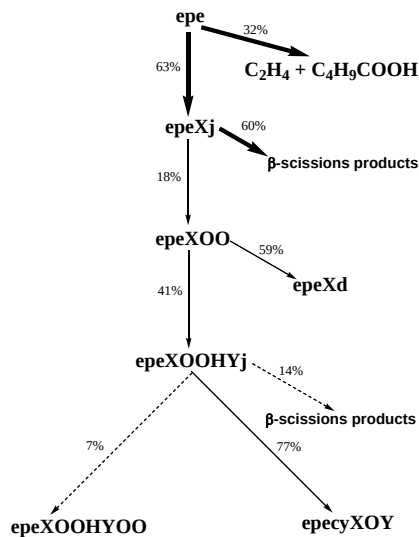


Figure 4.4: Reaction pathways from the kinetic modelling of ethyl valerate oxidation in a JSR at $\phi = 1$, $P = 10$ atm at 830 K [11].

valerate over a range of equivalence ratios ($\phi = 0.7 - 1.4$) and pressures (1, 3, 5

and 10 bar). The same kinetic mechanism validated against the ethyl valerate oxidation in a JSR was also validated against the laminar burning velocities for these conditions. The authors concluded that the laminar burning velocities at $\phi = 1$ varies as a function of $P^{-0.28}$.

A kinetic mechanism called "UCL" has been elaborated and validated against rich ethylene flames [66] and extended to the formation of oxygenated compounds involved in dimethoxymethane (methylal) combustion at low pressure [105, 106]. Sub-mechanisms for methylal ($C_3H_8O_2$) and ethylal ($C_5H_{12}O_2$) have also been tested against premixed rich ethylene flames added with methylal or ethylal [107]. Then, this mechanism has been extended to handle oxygenated species such as CH_2O (formaldehyde), C_2H_5OH (ethanol), CH_3CHO (acetaldehyde) and CH_3COOH (acetic acid); and validated at low pressure [108]. Finally, the "UCL" mechanism has been also tested and validated against rich benzene/ethanol ($C_6H_6/C_2H_5OH/O_2/Ar$) flames at low pressure, by studying the effect of this oxygenated compound on the soot precursors formation [65].

Recently, the present mechanism "UCL" was also validated on CH_3COCH_3 (acetone) added to $H_2/O_2/Ar$ flames at low pressure [109]. This improved mechanism was then, extended to the study of C_2H_5CHO (propanal) kinetics at low pressure [110].

To summarize, this UCL model has been tested against experimental flames of different fuels in order to check and improve its good reliability, at low pressure: CH_4 (methane), C_2H_2 (acetylene), C_2H_4 (ethylene), C_2H_6 (ethane), C_6H_6 (benzene), iC_4H_8 (isobutene), CH_2O (formaldehyde), CH_3CHO (acetaldehyde), CH_3COOH (acetic acid), $C_3H_8O_2$ (methylal), $C_5H_{12}O_2$ (ethylal), C_2H_5OH (ethanol), CH_3COCH_3 (acetone) and CH_3CH_2CHO (propanal).

The UCL mechanism is one of the few models able to simulate the combustion of species from C_1 to C_{10} , and of several oxygenated species. The model becomes more and more comprehensive with every new fuel study.

In this work, the UCL mechanism has been used to build a new improved kinetic model in combination with Dayma mechanism. This mechanism is suitable to model, with good agreement, the low pressure ethyl valerate premixed flat flames.

From ethyl valerate to the formation of C_4 species, the elementary reactions are taken from Dayma mechanism [11]. From C_4 to H_2/O_2 , the elementary

reactions used in this mechanism, are from the UCL model [111].

Moreover, some kinetic constants for the valeric acid decomposition have been modified to improve the new model. Table 4.4 illustrates the modifications of Dayma mechanism to improve the new kinetic model elaborated in this work. These modifications have been performed to reduce the maximum

Table 4.4: Rate constant modifications proposed to improve valeric acid (C_4H_9COOH) prediction, with $[BuCOOH-4=CH_3CHCH_2CH_2COOH; BuCOOH-3=CH_3CH_2CHCH_2COOH; BuCOOH-2=CH_3CH_2CH_2CHCOOH]$.

Authors	Reaction	A $cm^3/mol.s$	n	Ea cal/mol
1.Dayma [11]	$C_4H_9COOH + H=BuCOOH-4 + H_2$	1.30E+06	2.4	4.47E+03
This work	$C_4H_9COOH + H=BuCOOH-4 + H_2$	1.04E+07	2.4	4.47E+03
2.Dayma [11]	$C_4H_9COOH + H=BuCOOH-3 + H_2$	1.30E+06	2.4	4.47E+03
This work	$C_4H_9COOH + H=BuCOOH-3 + H_2$	7.80E+06	2.4	4.47E+03
3.Dayma [11]	$C_4H_9COOH + H=BuCOOH-2 + H_2$	1.30E+06	2.4	4.47E+03
This work	$C_4H_9COOH + H=BuCOOH-2 + H_2$	7.80E+06	2.4	4.47E+03
4.Dayma [11]	$C_4H_9COOH + O=BuCOOH-4 + OH$	4.77E+04	2.71	2.11E+02
This work	$C_4H_9COOH + O=BuCOOH-4 + OH$	1.908E+05	2.71	2.11E+02
5.Dayma [11]	$C_4H_9COOH + O=BuCOOH-3 + OH$	4.77E+04	2.71	2.11E+02
This work	$C_4H_9COOH + O=BuCOOH-3 + OH$	1.431E+05	2.71	2.11E+02
6.Dayma [11]	$C_4H_9COOH + O=BuCOOH-2 + OH$	4.77E+04	2.71	2.11E+02
This work	$C_4H_9COOH + O=BuCOOH-2 + OH$	1.431E+05	2.71	2.11E+02
7.Dayma [11]	$C_4H_9COOH + OH=BuCOOH-4 + H_2O$	4.68E+07	1.61	-3.5E+01
This work	$C_4H_9COOH + OH=BuCOOH-4 + H_2O$	1.872E+08	1.61	-3.5E+01
8.Dayma [11]	$C_4H_9COOH + OH=BuCOOH-3 + H_2O$	4.68E+07	1.61	-3.5E+01
This work	$C_4H_9COOH + OH=BuCOOH-3 + H_2O$	1.404E+08	1.61	-3.5E+01
9.Dayma [11]	$C_4H_9COOH + OH=BuCOOH-2 + H_2O$	4.68E+07	1.61	-3.5E+01
This work	$C_4H_9COOH + OH=BuCOOH-2 + H_2O$	1.404E+08	1.61	-3.5E+01

mole fraction of valeric acid (C_4H_9COOH) in the flames, overestimated in the original model proposed by Dayma et al. [11]. The objective was to accelerate the consumption of C_4H_9COOH . The present values of A constant have been obtained by trial and error. The original values were from Dayma mechanism [11], and then we tested other constants from the literature to improve the simulated mole fraction of different intermediate species, but without success.

Finally, we opted for keeping Dayma's values for the activation energy (E_a) and the temperature coefficient (n), and only for changing the values of A , in the Arrhenius equation (Table 4.4).

To improve the simulated mole fraction profiles of formic acid (HOCHO), the following reactions have been added from the Aramco mechanism proposed by Metcalfe et al. [112]:

- $\text{HOCHO} + \text{OH} = \text{CO}_2 + \text{H}_2\text{O} + \text{H}$
- $\text{CH}_3\text{CHO} + \text{OH} = \text{CH}_3 + \text{HOCHO}$
- $\text{CH}_2\text{O} + \text{OH} = \text{HOCHO} + \text{H}$

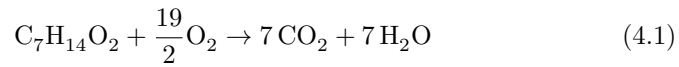
The complete kinetic model contains 480 chemical species and 2740 elementary reactions. To reduce the mechanism complexity for calculations, the mechanism has been simplified by eliminating all the low temperature chemical reactions and the species included in these reactions. Then, all the chemical species with concentrations lower than 10^{-10} and the chemical reactions involved have been removed.

The simplified mechanism contains 211 chemical species and 1368 elementary reactions. It is presented in appendix B and named "Katshiatschia mechanism". It converges ten times faster than the complete mechanism.

4.2 Elemental balance

The experimental mole fractions of the fuel, oxidizer and products are used to determine the combustion balance of the three ethyl valerate flames.

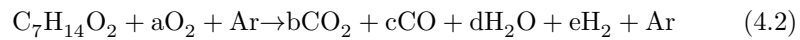
The stoichiometric equation of ethyl valerate combustion is:



In Equation (4.1), the ethyl valerate combustion is complete and leads to the formation of CO_2 and H_2O only.

In the case of the studied flames, the input chemical species are: $\text{C}_7\text{H}_{14}\text{O}_2$ (fuel), O_2 (oxidizer) and Ar (diluent). After combustion, the main molecules produced are: H_2O , CO_2 , CO and H_2 .

Basically, the combustion of ethyl valerate can be written using the following chemical reaction:



To determine the carbon, hydrogen and oxygen combustion balance, all these major species have to be taken into account. Equation (4.3) is used to determine the balance, using the mole fractions of the different chemical compounds before and after the combustion.

$$\left(\frac{X_i}{X_{Ar}}\right)_{input} / \left(\frac{X_i}{X_{Ar}}\right)_{output} \quad (4.3)$$

where X_i presents the mole fraction of species i and X_{Ar} is the argon mole fraction.

Argon is used as a diluent in the combustion. Its mole fraction concentrations are reduced throughout the flame due to the increase of the number of moles in the burned gases. This has no impact on the ratios defined in Equation (4.3). The balance is calculated by considering each atom involved in the ethyl valerate combustion. For the input parameters, X_i is calculated using Equations (4.4), (4.5) and (4.6), taking into account $C_7H_{14}O_2$ and O_2 :

$$X_C = 7 \times X_{C_7H_{14}O_2} \quad (4.4)$$

$$X_H = 14 \times X_{C_7H_{14}O_2} \quad (4.5)$$

$$X_O = 2 \times X_{C_7H_{14}O_2} + 2 \times X_{O_2} \quad (4.6)$$

where X_i is the input mole fraction of the species used.

For the output parameters, X_i is calculated using Equations (4.7), (4.8) and (4.9), for the products : CO, CO₂, H₂ and H₂O.

$$X_C = X_{CO_2} + X_{CO} \quad (4.7)$$

$$X_H = 2 \times X_{H_2O} + 2 \times X_{H_2} \quad (4.8)$$

$$X_O = 2 \times X_{CO_2} + X_{CO} + X_{H_2O} + 2 \times X_{O_2} \quad (4.9)$$

Where X_{CO_2} , X_{CO} , X_{H_2O} , X_{O_2} and X_{H_2} are the output mole fraction of carbon dioxide, carbon monoxide, water, oxygen and hydrogen after the ethyl valerate combustion.

The concentration for the balance calculations are depicted in Table 4.5.

Equation (4.3) is used to calculate the balance of each atom of carbon, hydrogen and oxygen in the three studied flames and the results are given in Table 4.6. According to the results shown in Table 4.6, the carbon balance is equal

Table 4.5: Experimental and simulated (*) input and output mole fractions used in the balance calculations.

Species	Input	(1 mm)			Output (20 mm)		
		mole fraction			mole fraction		
		$\phi = 0.81$	$\phi = 0.95$	$\phi = 1.31$	$\phi = 0.81$	$\phi = 0.95$	$\phi = 1.31$
C ₇ H ₁₄ O ₂	0.037	0.038	0.039	0	0	0	0
O ₂	0.406	0.357	0.276	0.060	0.036	0	0
CO ₂	0	0	0	0.162	0.145	0.094	0.094
CO	0	0	0	0.045	0.064	0.123	0.123
H ₂ O	0	0	0	0.189	0.178	0.154	0.154
H ₂	0	0	0	0.012	0.016	0.038	0.038
Ar	0.521	0.577	0.672	0.439	0.478	0.537	0.537
H(*)	0	0	0	0.0167	0.0162	0.0202	0.0202
O(*)	0	0	0	0.01741	0.0132	0.0040	0.0040
OH(*)	0	0	0	0.0231	0.0242	0.0128	0.0128

Table 4.6: Balance results in the three experimental ethyl valerate flames.

ϕ	Carbon	Hydrogen	Oxygen
$\phi = 0.81$	0.95	0.93	0.86
$\phi = 0.95$	0.95	0.89	0.88
$\phi = 1.31$	0.99	0.88	0.92

to unity in the rich flame and 0.96 in the stoichiometric and lean flames. The oxygen balance is equal to 0.86, 0.88 and 0.92 in the lean, stoichiometric and rich flames, respectively. For the hydrogen balance, the calculated values are 0.93, 0.89 and 0.88 in the lean, stoichiometric and rich flames, respectively. These lower values for hydrogen and oxygen balances may be due to the mole fraction of radicals such as H, OH and O not taken into account in the experimental balance calculations. These radicals are formed during combustion and the simulated mole fraction profiles are presented in Figures 4.5 - 4.8. Figure 4.5 shows that the H radical is a main radical with a maximum concentration of 0.02 in the rich flame. In the lean flame, the maximum concentration is 0.016; and 0.015 in the stoichiometric flame. This radical has to be considered as a product of the ethyl valerate combustion due to the simulated profiles in the

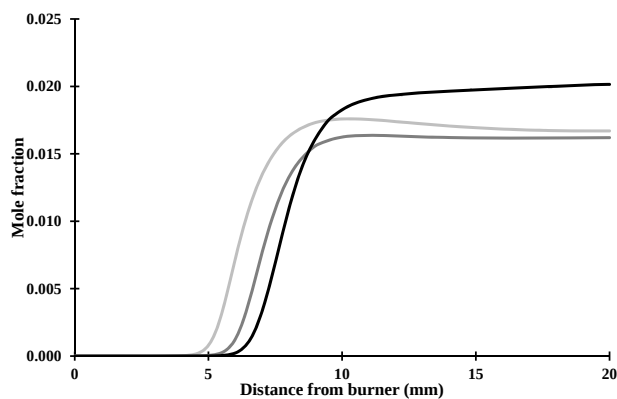


Figure 4.5: Simulated mole fraction profiles of H radical in rich (black solid line), stoichiometric (grey solid line) and lean (light grey solid line) ethyl valerate flames.

three flames. For this reason, its concentrations must be taken into account for the hydrogen balance.

The OH radical is also a major radical formed during ethyl valerate combus-

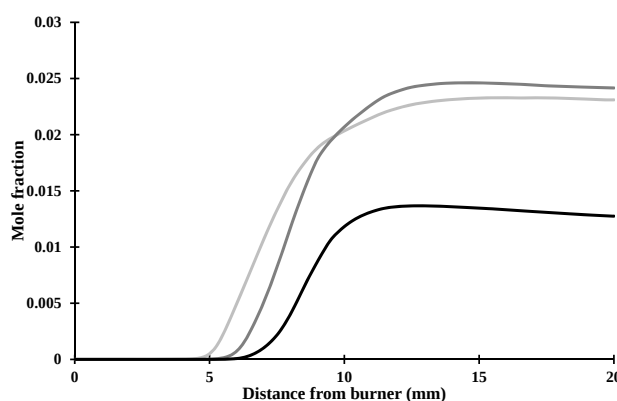


Figure 4.6: Simulated mole fraction profiles of OH in rich (black solid line), stoichiometric (grey solid line) and lean (light grey solid line) ethyl valerate flames.

tion. Its maximum concentration is 0.025, 0.023 and 0.014 in the stoichiometric, lean and rich flames, respectively. As depicted in Figure 4.6, its mole fraction concentrations must also be taken into account for the hydrogen and oxygen balances.

The O radical has a higher concentration in the lean flame (0.016) than in the stoichiometric one (0.014), than in the rich flame (0.004). In the rich flame, the oxygen balance is quite high (0.92). This means that the O radical is more

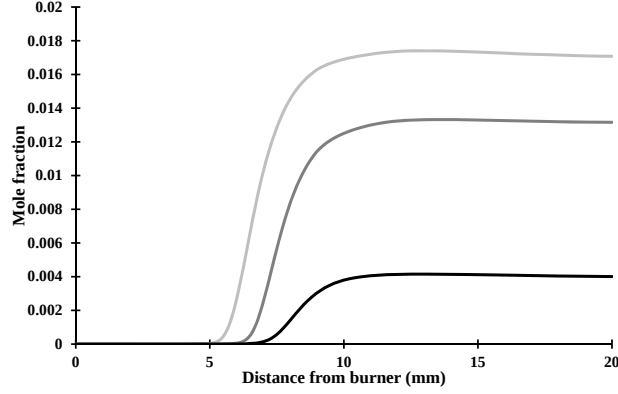


Figure 4.7: Simulated mole fraction profiles of O radical in rich (black solid line), stoichiometric (grey solid line) and lean (light grey solid line) ethyl valerate flames.

involved in the stoichiometric and lean flames.

Its concentrations have to be used in the calculations of the O balance in the three flames, even if in the rich flame its involvement is limited.

Finally, the HO_2 radical is formed and consumed during ethyl valerate com-

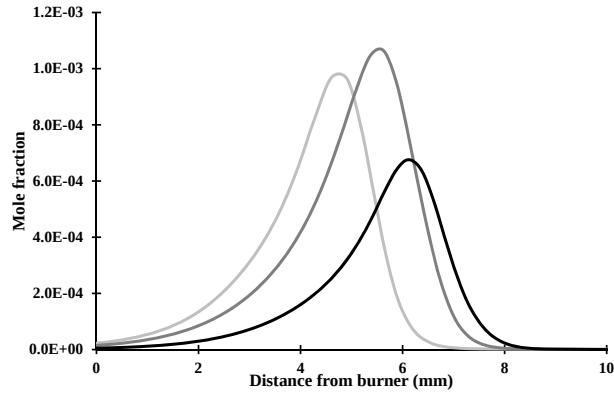


Figure 4.8: Simulated mole fraction profiles of HO_2 radical in rich (black solid line), stoichiometric (grey solid line) and lean (light grey solid line) ethyl valerate flames.

bustion in the three flames as depicted in Figure 4.8. Its concentrations do not influence any balance calculation due to its total consumption in the post combustion zone.

For the simulated mole fraction values, the balance of carbon, oxygen and hydrogen is equal to 1 (mass balance from the software). The calculation of carbon, hydrogen and oxygen balances using the simulated data for H, OH and

O and the experimental ones for O_2 , CO, CO_2 , H_2 , H_2O and Ar is reported in Table 4.7. Only the hydrogen and carbon balances are equal to 1 in the lean

Table 4.7: Balance calculated from experimental and simulated data in the three ethyl valerate flames.

ϕ	Carbon	Hydrogen	Oxygen
$\phi = 0.81$	0.95	1.00	0.96
$\phi = 0.95$	0.95	0.97	0.98
$\phi = 1.31$	0.99	0.96	0.96

and the rich flames, respectively. The other balances are between 0.95 and 0.98. The experimental error on the calibrated concentrations could explain these results.

4.3 Ethyl valerate flame structures

Three ethyl valerate flat flames have been stabilized on a burner at low pressure (55 mbar), at three equivalence ratios ($\phi = 0.81 - 0.95$ and 1.31). The gas chromatography is used to separate and quantify, after calibration, different chemical compounds formed during ethyl valerate combustion. The analyzed species (fuel, oxidizer, diluent, intermediate species and products) are presented in Table 2.5. In this section, we present the experimental results in comparison with the simulated ones obtained by the model elaborated in this work. The simulations have been performed using the *Cosilab*® software [12].

4.3.1 Major species

The ethyl valerate flames are stabilized at different equivalence ratios ($\phi = 0.81$, 0.95 and 1.31). The main species are : fuel (EPE), oxidizer (O_2), and products such as (H_2 , CO, CO_2 and H_2O).

Fuel and oxidizer

The experimental mole fraction profiles of the fuel and of the oxidizer compared to the simulated ones in the three flames are depicted in Figures 4.9 and 4.10. The simulated mole fraction profiles of EPE and O_2 are in a good agreement with the experimental ones (Figures 4.9 and 4.10). For the ethyl valerate, the

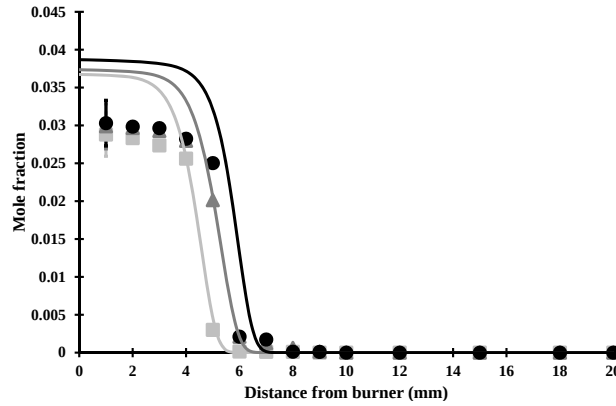


Figure 4.9: Experimental (symbols) and simulated (solid lines) mole fraction profiles of ethyl valerate in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

highest experimental concentrations are 0.030, 0.029 and 0.028 in the rich, stoichiometric and lean flames, respectively. In the simulations, the highest ethyl valerate concentrations are 0.039, 0.038 and 0.037 in the rich, stoichiometric and lean flames, respectively. From these values, there is a loss of 23.07% between the simulated and experimental concentrations. As the experimental error for this species is evaluated at 10%, the difference between these values should be lower than 23%. Experimentally, ethyl valerate probably condenses after the compression system, due to the rapid expansion of the gases to bring them to atmospheric pressure, before their injection into the GC. This condensation would be observed mainly for the fresh gases where the concentration is maximum. Moreover, for the three ethyl valerate mole fraction profiles, the differences between the simulated and the experimental concentration are similar. This indicates that in the fresh gases zone, the same amount of ethyl valerate condenses during the compression.

In Figure 4.10, the simulated mole fraction profiles of oxygen are well predicted compared to the experimental ones. Taking the experimental error of 5% into account, the highest experimental concentration of O_2 is 0.276, 0.357 and 0.406 for the rich, stoichiometric and lean flames, respectively. For the simulated ones, this concentration is 0.282, 0.379 and 0.435 for the rich, stoichiometric and lean flames, respectively. The difference of concentrations between these values is about 2.2, 5.8 and 6.7% in the rich, stoichiometric and lean flame, respectively.

As depicted in Figures 4.9 and 4.10, the effect of the equivalence ratio is well

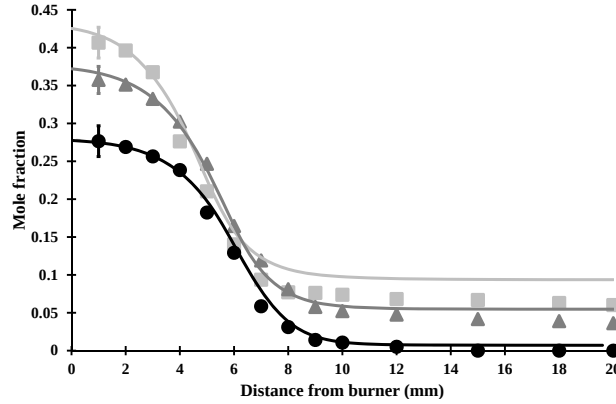


Figure 4.10: Experimental (symbols) and simulated (solid lines) mole fraction profiles of oxygen in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

simulated compared to the experimental data in all investigated flames for the fuel and the oxidizer.

Some O_2 remains in the burned gases in the lean and stoichiometric flames (Figure 4.10), due to the equivalence ratio.

Based on the simulated and the experimental mole fraction profiles of EPE and O_2 , the front flame is located between 4 and 6 mm from the burner.

Diluent

Argon is used as a diluent in the composition of the three investigated ethyl valerate flames. This choice is promoted by the fact that argon is a neutral gas and cannot react with the species included in the ethyl valerate combustion. Figure 4.11 illustrates the comparison between the simulated and the experimental mole fraction profiles of argon in the three flames. The experimental error is 5% for argon, due to this error, the simulated mole fraction profiles are in a good agreement with the experimental ones. The argon mass flow rate must remain constant throughout the flame. The slight decrease observed in the experimental mole fraction profiles is due to the increase of the number of moles during the combustion. This phenomenon is well simulated.

Products

Figures 4.12, 4.13, 4.14 and 4.15 show the simulated and the experimental mole fraction profiles of the main products such as CO_2 , CO , H_2 and H_2O for the

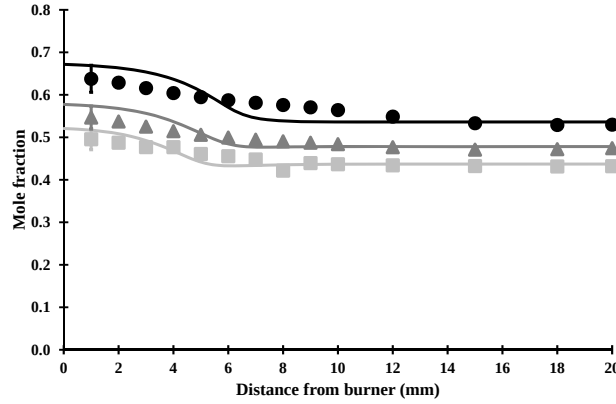


Figure 4.11: Experimental (symbols) and simulated (solid lines) mole fraction profiles of argon in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

three investigated flames.

The experimental error is 5% for carbon monoxide, carbon dioxide and water and it is 10% for the hydrogen due to its diffusion in the flame.

The experimental mole fraction profiles of CO_2 are very well simulated by the model elaborated in this work (Figure 4.12). The concentrations of CO_2 in the burned gases at 20 mm are: 0.094, 0.145 and 0.162 (experimentally) and 0.096, 0.141 and 0.162 (numerically) in the rich, stoichiometric and lean flames, respectively.

The effect of the equivalence ratio is also well simulated and well observed experimentally. The CO_2 concentrations are lower in the rich flame than in the other flames. CO_2 is mainly produced in the flame front.

The main carbon dioxide formation is performed in the three flames via the chemical reaction shown in Equation (4.10), with a contribution of 56, 65 and 67% in the rich, stoichiometric and lean flames, respectively.



Also, 19, 13 and 11% of CO_2 is produced from CH_2 in the rich, stoichiometric and lean flames, respectively as shown in Equation (4.11).



The experimental and the simulated mole fraction profiles of CO are depicted

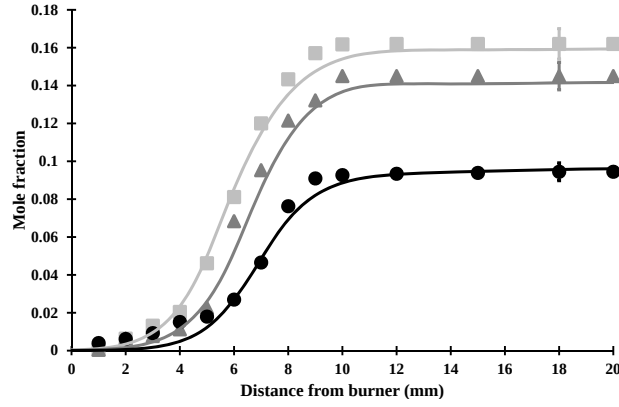


Figure 4.12: Experimental (symbols) and simulated (solid lines) mole fraction profiles of carbon dioxide in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

in Figure 4.13. The simulated mole fraction profiles agree well the experimental ones. In the burned gases, the CO mole fractions are: 0.123, 0.064 and 0.045 (experimentally) and 0.120, 0.074 and 0.054 (numerically) at 1.31, 0.95 and 0.81 equivalence ratios, respectively. In the stoichiometric and the lean flames, CO is produced and consumed in the flame front and then remains in the burned gases. In the rich flame, it is formed throughout the flame. CO is

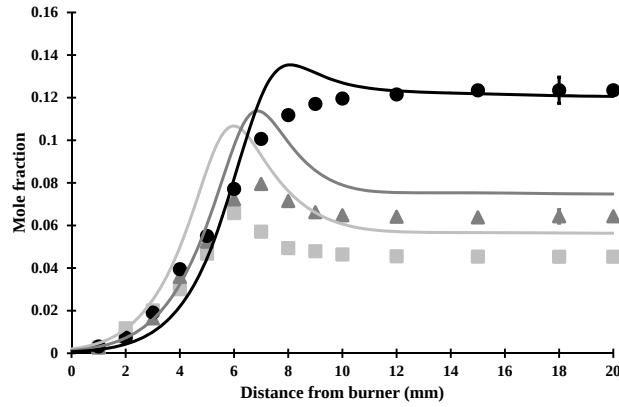
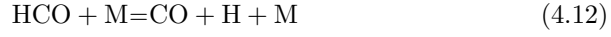


Figure 4.13: Experimental (symbols) and simulated (solid lines) mole fraction profiles of carbon monoxide in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

produced in the three flames from HCO consumption with a contribution of 22, 16 and 14% (Equation (4.12)), and 14, 25 and 30% (Equation (4.13)) in

the rich, stoichiometric and lean flames, respectively.



In the rich flame, 96% of CO consumption produces CO₂, and 97% in the stoichiometric and lean flames, respectively (Equation (4.10)).

Figure 4.14 presents the experimental and simulated mole fraction profiles of H₂. When the high concentrations are reached, the three simulated profiles present a good agreement with the experimental ones. The gap in the fresh gases zone, may be due to the diffusion effect of hydrogen with a strong impact on low concentrations. This diffusion effect is taken into account in the numerical simulation using *Cosilab*® [12] software as described in Chapter 3. H₂ is produced and slightly consumed in the flame front. It remains stable in the burned gases.

The experimental and the simulated mole fraction profiles of H₂O are in a

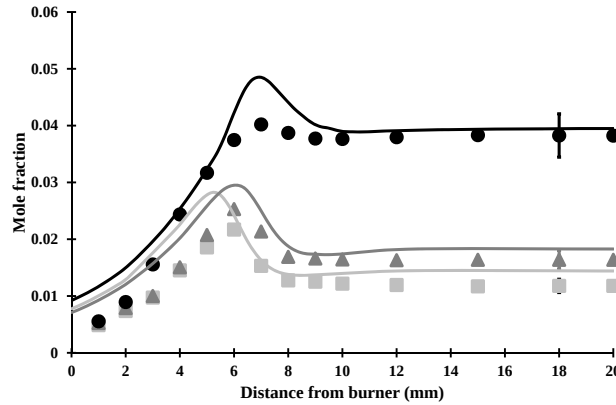


Figure 4.14: Experimental (symbols) and simulated (solid lines) mole fraction profiles of hydrogen in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

very good agreement as seen in the results presented in Figure 4.15 for the three flames. The experimental H₂O mole fraction profiles were determined by combining experimental results and theoretical values using the water gas shift reaction (4.14):



From Equation (4.14), the equilibrium constant (K_P) can be defined as shown in Equation (4.15):

$$K_P = \frac{P_{CO_2} \times P_{H_2}}{P_{CO} \times P_{H_2O}} \quad (4.15)$$

From Equation (4.15), K_P can be determined in terms of logarithm as depicted in Equation (4.16):

$$\log(K_P) = \log(K_{p,CO_2}^0(T)) + \log(K_{p,H_2}^0(T)) - \log(K_{p,CO}^0(T)) - \log(K_{p,H_2O}^0(T)) \quad (4.16)$$

This correction is very important because, experimentally, it is impossible to perform the calibration of water. The corresponding coefficients at these high temperatures for $\log(K_{p,CO_2}^0(T))$, $\log(K_{p,CO}^0(T))$ and $\log(K_{p,H_2O}^0(T))$ are presented in the work of Chase M.W. Jr. et al. [113].

The molar concentration of H_2O is then calculated from Equation (4.15) at 25 mm from the burner at constant pressure and temperature, after simplification:

$$[H_2O] = \frac{[CO_2][H_2]}{[CO]K_P} \quad (4.17)$$

The maximum experimental concentration is 0.154, 0.178 and 0.189 for the rich, stoichiometric and lean flames, respectively. The simulated values are 0.163, 0.178 and 0.184 for the rich, stoichiometric and lean flames, respectively. The equivalence ratio effect is very well observed for the three flames. The leanest flames have a higher H_2O mole fractions than the richest ones.

H_2O is mainly formed in the flame front and then remains constant along the flame.

4.3.2 Oxygenated compounds

The simulated mole fraction profiles of the oxygenated species such as valeric acid (C_4H_9COOH), acetaldehyde (CH_3CHO), formaldehyde (CH_2O), acetone (CH_3COCH_3) and formic acid ($HOCHO$) compared with the experimental ones are depicted in Figures 4.16 - 4.20. The experimental errors are estimated at 20% for the species such as acetaldehyde and formaldehyde and, at 25% for valeric acid, acetone and formic acid.

The simulated valeric acid (C_4H_9COOH) mole fraction profiles present a good agreement with the experimental ones in the lean and rich flames (Figure 4.16). In the stoichiometric flame, the simulated mole fraction profile of this oxy-

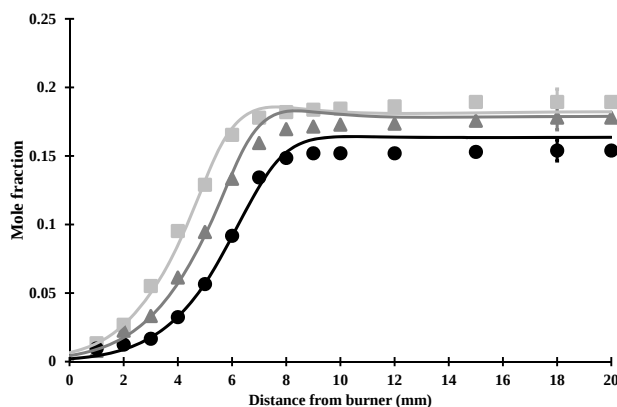


Figure 4.15: Experimental (symbols) and simulated (solid lines) mole fraction profiles of H_2O in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

generated species is overestimated by the model. The balance between the species involved in the production and the consumption of this acid could be responsible for this discrepancy. Indeed, in the stoichiometric flame, valeric acid is produced from EPE from the reaction: $EPE = C_4H_9COOH + C_2H_4$. For its consumption, the valeric acid reacts with H radical with a contribution of 77% to produce the $BuCOOH-4$ radical ($C_4H_9COOH + H = CH_3CHCH_2CH_2COOH + H_2$). At the flame front where the intermediate species have a maximum concentration, the following concentrations are calculated: 1.69×10^{-4} and 6.93×10^{-5} for H radical, 1.72×10^{-4} and 5.99×10^{-4} for the valeric acid and finally 1.41×10^{-2} and 1.9×10^{-2} for ethyl valerate in the lean and stoichiometric flames, respectively. In the stoichiometric flame, there is more ethyl valerate and less H radical concentrations than in the lean one, leading to an overestimated mole fraction profile of valeric acid in the simulations. This may be the reason of the disagreement between simulation and experiments in the stoichiometric profile. We attribute this phenomenon to the difference between the concentrations of the evolved species according to the equivalence ratio. To check this statement, the same comparison is realized with the experimental data and it is noticed that: 0.003 mole fraction of EPE is observed at the same distance in the lean flame (4.6 mm) for 0.0201 in the stoichiometric flame (5 mm). So, the consumption of ethyl valerate in the stoichiometric is lower than in the lean flame. The best way to solve this problem would be to measure, experimentally, the mole fraction of H radicals. The GC method, does not allow to perform the analysis of radicals.

Valeric acid is a reactive chemical compound due to its carboxylic function and the experimental measurements are quite difficult. Indeed, this molecule can react before the GC entrance. In the three flames, valeric acid is produced

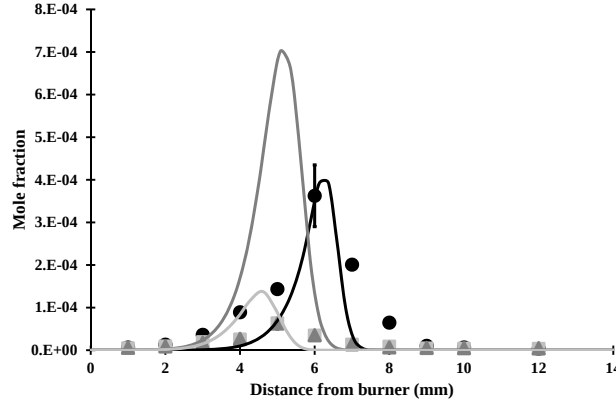
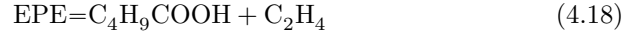


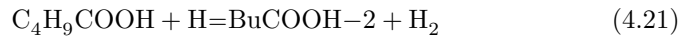
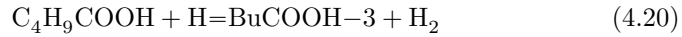
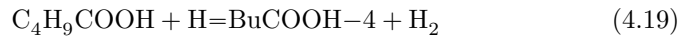
Figure 4.16: Experimental (symbols) and simulated (solid lines) mole fraction profiles of valeric acid in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

from ethyl valerate with a contribution of 100% (Equation (4.18)).



The $\text{C}_4\text{H}_9\text{COOH}$ consumption leads to the formation of:

- $\text{BuCOOH}-4$ ($\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOH}$)
- $\text{BuCOOH}-3$ ($\text{CH}_3\text{CH}_2\text{CHCH}_2\text{COOH}$)
- $\text{BuCOOH}-2$ ($\text{CH}_3\text{CH}_2\text{CH}_2\text{CHCOOH}$)



In the rich flame, this consumption is led by a contribution of 33% for Equation (4.19) and 25% for Equations (4.20) and (4.21). In the stoichiometric flame, it is 29% for Equation (4.19) and 22 % for Equations (4.20) and (4.21); and 28% for Equation (4.19) and 21% for Equations (4.20) and (4.21) in the lean one.

The simulated mole fraction profiles of acetaldehyde (CH_3CHO) agree well with the experimental profiles in the three EPE flames (Figure 4.17). Its maximum concentration is higher in the lean and the stoichiometric flames than in the rich one. The consequence of its production will be discussed later with the EPE consumption pathways in the lean flame. The formation of acetaldehyde is

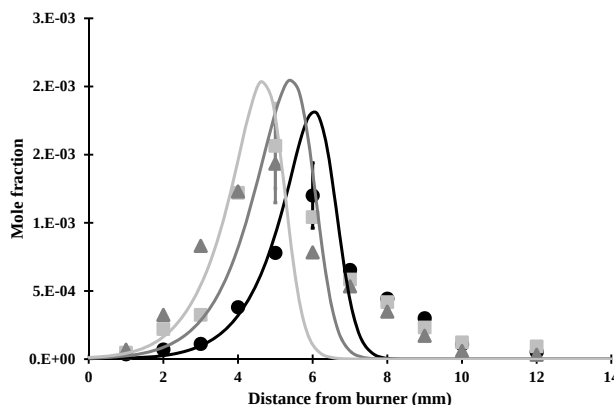
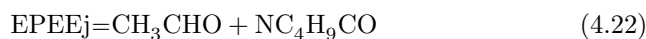


Figure 4.17: Experimental (symbols) and simulated (solid lines) mole fraction profiles of acetaldehyde in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

mainly led in the three flames by the radicals EPEEj ($\text{CH}_3(\text{CH}_2)_3\text{COOCHCH}_3$) and $\text{CH}_3\text{CH}_2\text{O}$ (Equations (4.22) and (4.23)).

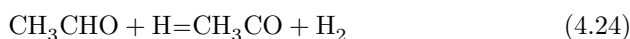


Acetaldehyde is produced from EPEEj with a contribution of 49, 44 and 43% in the rich, stoichiometric and lean flames.

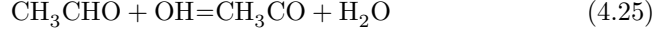


The formation of acetaldehyde from the $\text{CH}_3\text{CH}_2\text{O}$ radical (Equation (4.23)) has a contribution of 17, 16 and 15%, in the rich, stoichiometric and lean flames, respectively.

The consumption of acetaldehyde produces the radical CH_3CO and H_2 (Equation (4.24)) with a contribution of 83, 75 and 71% in the rich, stoichiometric and lean flames, respectively:



In the stoichiometric and lean flames, 11 and 17% of acetaldehyde consumption lead to the formation of CH_3CO and H_2O , respectively as shown in Equation (4.25).



The simulated mole fraction profiles of formaldehyde (CH_2O) are shifted by 1 mm away to the fresh gases in comparison with the experimental ones, as in the case of H_2 (Figure 4.18). However, the agreement between the simulated and the experimental mole fraction profiles of this species is good in the investigated ethyl valerate flames. The equivalence ratio effect is in agreement in the simulated and experimental mole fraction profiles. The formaldehyde

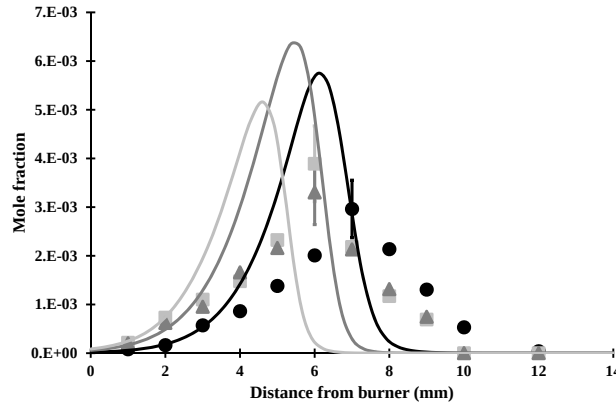
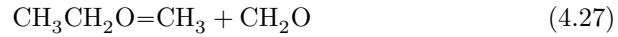


Figure 4.18: Experimental (symbols) and simulated (solid lines) mole fraction profiles of formaldehyde in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

is mainly produced in the three flames by the radical C_2H_3 (Equation (4.26)) with a contribution of 50, 50 and 49% in the rich, stoichiometric and lean flame, respectively:

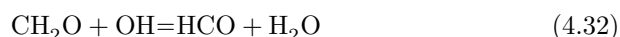


In the rich flame, 11% of formaldehyde is produced from $\text{CH}_3\text{CH}_2\text{O}$, CH_3 and CH_2 (Equations (4.27), (4.28) and (4.29)).



In the stoichiometric and lean flames, 12% of formaldehyde is produced via Equation (4.27). Then, 10% of CH_2O is produced, in both flames, via Equations (4.28) and (4.29).

The consumption of formaldehyde with O radical produces the HCO radical with the contributions in the rich flame: 47%, the stoichiometric flame: 58% and the lean flame: 62% (Equation (4.30)). With H radical, the contributions are in rich flame: 22%, stoichiometric flame: 12% and lean flame: 10% (Equation (4.31)). Finally with OH radical, the contribution are in rich flame: 16%, stoichiometric flame: 20% and lean flame: 20% (Equation (4.32)).



The other oxygenated species analyzed in this study are CH_3COCH_3 (acetone) and HOCHO (formic acid). The simulated profiles compared to the experimental ones are illustrated in Figures 4.19 and 4.20, respectively. As depicted in Figure 4.19, the mechanism underestimates the acetone mole fraction profile with approximately a factor of 2 in the stoichiometric and the rich flames. The agreement between the experimental and the simulated mole fraction profiles is good in the lean flame.

Moreover, for the formic acid, the mechanism overestimates the three mole fraction profiles, by a factor of 2 for the lean and the stoichiometric flames. However, the concentrations of the both species are lower than 100 ppm and their experimental errors are estimated at 20%.

Acetone is produced by the reaction between CH_3CHO and CH_3CO in the three investigated flames (Equation (4.33)).



The contribution of this reaction is 22, 25 and 23% in the rich, stoichiometric and lean flames, respectively.

The acetone consumption, reacting with H radical, leads to the formation of the CH_3COCH_2 radical (Equation (4.34)) with the contribution in rich flame: 57%, stoichiometric flame: 43% and lean flame: 37% and with OH radical

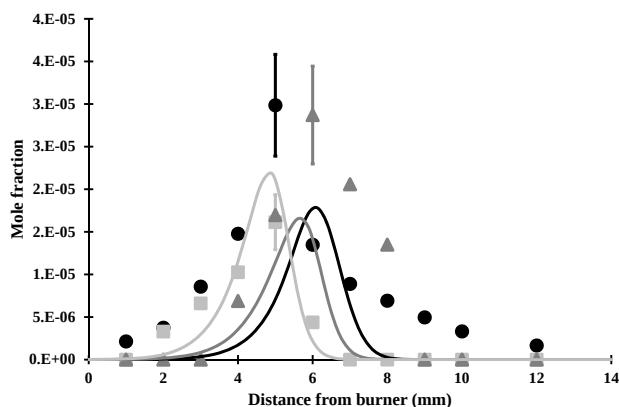


Figure 4.19: Experimental (symbols) and simulated (solid lines) mole fraction profiles of acetone in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

(Equation (4.35))(rich flame: 24%, stoichiometric flame: 38% and lean flame: 43%):

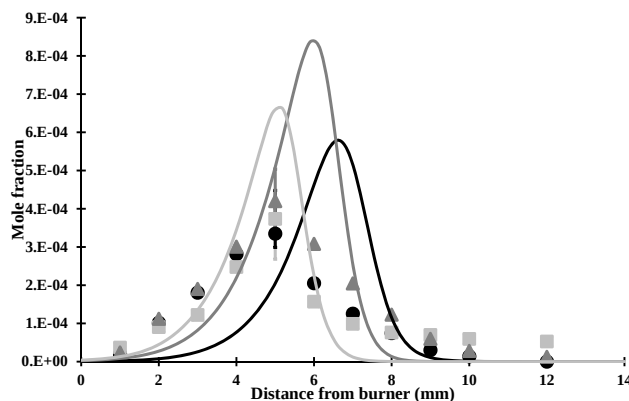
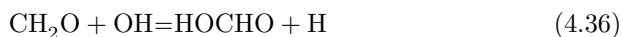


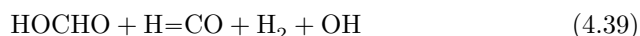
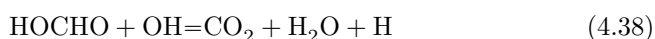
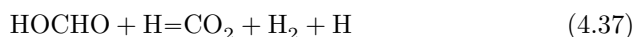
Figure 4.20: Experimental (symbols) and simulated (solid lines) mole fraction profiles of formic acid in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

The chemical reaction between CH_2O and OH radical (Equation (4.36)) leads to the formation of formic acid in the three flames with a contribution of

96, 92 and 89% in the rich, stoichiometric and lean flame, respectively:



The formic acid consumption's chemical reactions are presented in Equations (4.37), (4.38) and (4.39).



In the rich flame, the contributions are 45, 27 and 20% for these three reactions, respectively. Then, in the stoichiometric flame, they are 39, 31 and 10% and finally in the lean flame, 43, 27 and 10%.

4.3.3 Hydrocarbon compounds

Figures 4.21, 4.22 and 4.23 show the experimental and the simulated mole fraction profiles of ethylene (C_2H_4), methane (CH_4) and acetylene (C_2H_2) in the three ethyl valerate flames. The experimental error is evaluated at 20% for ethylene and methane, but it is estimated at 25% for acetylene due to its low sensitivity to the columns used in this work.

The hydrocarbon compounds measured in the lean and stoichiometric flames, are C_2H_4 and CH_4 . Their simulated mole fraction profiles agree with the experimental data as related in Figures 4.21 and 4.22. For C_2H_4 and CH_4 , the effect of the equivalence ratio is well caught in both ethyl valerate flames. The experimental and the simulated maximum concentrations are higher in the stoichiometric than in the lean flame.

In the rich flame, for the hydrocarbons (C_2H_4 , CH_4 and C_2H_2), the model predictions are validated by the experimental data as depicted in Figures 4.21, 4.22 and 4.23. However, the kinetic model underestimates the C_2H_4 concentration and overestimates the C_2H_2 one, as shown in Figures 4.21 and 4.23, respectively.

The equivalence ratio effect is well simulated in comparison to the experimental data. Rich ethyl valerate flame produces higher hydrocarbons concentrations than stoichiometric and lean flames, successively. It should be noted that C_2H_2 appears in the rich flame but not in the stoichiometric and the lean flames.

Experimentally, it was not possible to quantify the concentration of acetylene in the two other flames, due to its too low concentrations. The CPSIL-5CB column used during the GC analysis, is not very sensitive to this molecule. According to simulations, the C_2H_2 concentrations in lean and stoichiometric flames are lower than 100 ppm. In the rich flame, the production of ethylene is

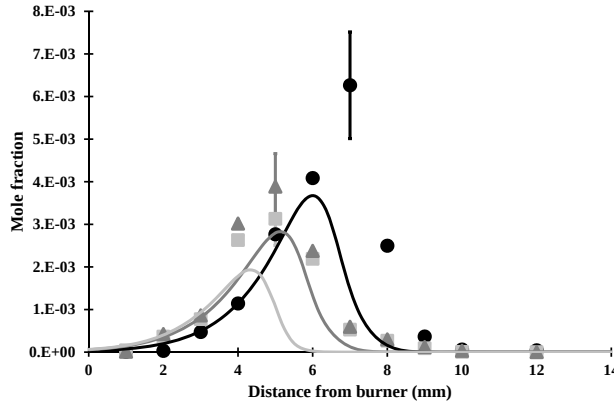
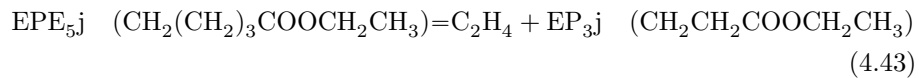
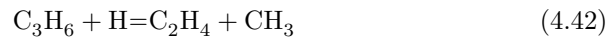
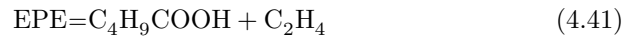
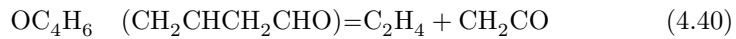
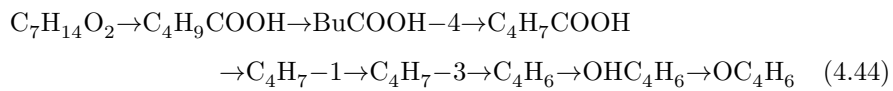


Figure 4.21: Experimental (symbols) and simulated (solid lines) mole fraction profiles of ethylene in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

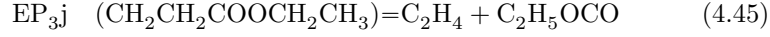
due to four main reactions as depicted in Equations (4.40), (4.41), (4.42), and (4.43) with contributions of 14, 13, 12 and 11%, respectively.



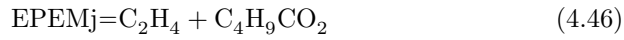
OC_4H_6 is produced from $C_7H_{14}O_2$ (EPE) as depicted in Equation (4.44).



In the stoichiometric flame, ethylene is produced from Equations (4.40), (4.45) and (4.41) with a contribution of 14, 11 and 10%, respectively.



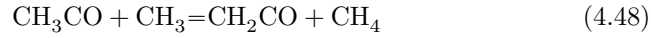
The production of ethylene, in the lean flame, is led by the dissociation of EPE_{5j} (Equation (4.40)), EP_{3j} (Equation (4.45)) and EPEMj ($(\text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2)$ (Equation (4.46)) with a contribution of 16, 12 and 10%, respectively.



The ethylene is consumed in the three flames (Equation (4.47)) with a contribution of 97% to produce C_2H_3 and H_2 :



Methane is produced from the CH_3CO and CH_3 radicals in the three investigated flames (Equations (4.48), (4.49) and (4.50)).



In the rich flame, the methane is produced with a contribution of 41, 17 and 16%, by Equations (4.48), (4.49) and (4.50), respectively. In the stoichiometric flame, the contribution for the same reactions is 42 (Equation (4.48)), 21 (Equation (4.49)) and 17% (Equation (4.50)), respectively. Finally, in the lean flame, the contribution is 41, 23 and 18% in Equations (4.48), (4.49) and (4.50), respectively. The methane consumption produces the CH_3 radical by reacting with H , OH and O radicals (Equations (4.51), (4.52) and (4.53)).



The contribution in consumption of methane is 55% (Equation (4.51)), 33%

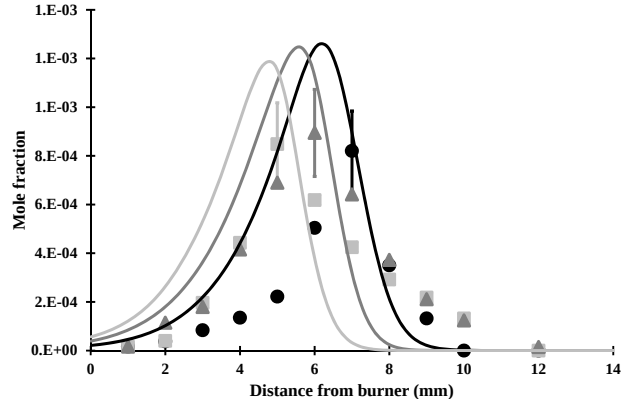


Figure 4.22: Experimental (symbols) and simulated (solid lines) mole fraction profiles of methane in rich (black circles), stoichiometric (grey triangles) and lean (light grey squares) ethyl valerate flames.

(Equation (4.52)) and 11% (Equation (4.53)) in the rich ; 43% (Equation (4.51)), 35% (Equation (4.52)) and 21% (Equation (4.53)) in stoichiometric and 46% (Equation (4.51)), 30% (Equation (4.52)) and 24% (Equation (4.53)) in lean ethyl valerate flames, respectively.

Acetylene is produced in the three ethyl valerate flames by the C_2H_3 radical

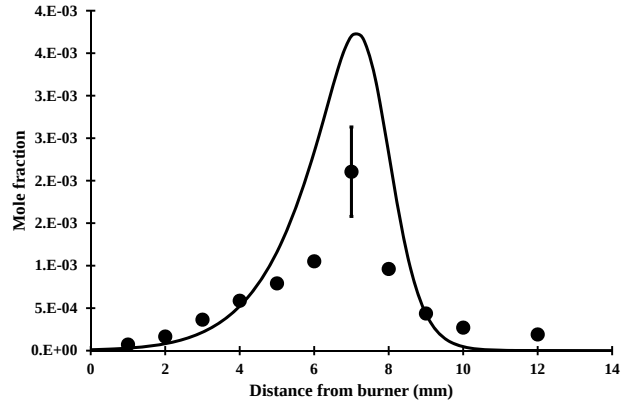
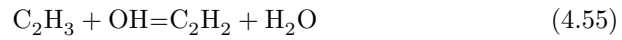


Figure 4.23: Experimental (symbols) and simulated (solid lines) mole fraction profiles of acetylene in rich ethyl valerate flame.

reacting with H and OH radicals (Equations (4.54) and (4.55)).



The contribution in formation of acetylene is 23% (Equation (4.54)) and 13% (Equation (4.55)) in the rich, 24% (Equation (4.54)) and 27% (Equation (4.55)) in the stoichiometric, and finally 31% (Equation (4.55)) and 23% (Equation (4.54)) in the lean ethyl valerate flames.

Then, acetylene reacts with O radical to produce HCCO (Equation (4.56)) and CH₂ (Equation (4.57)).



In the rich flame, the contribution in consumption of acetylene is 59% (Equation (4.56)) and 31% (Equation (4.57)). This contribution is 62% (Equation (4.56)) and 32% (Equation (4.57)) in the stoichiometric flame. In the lean ethyl valerate flame, it is 63% (Equation (4.56)) and 32% (Equation (4.57)).

4.4 Ethyl valerate simulated combustion pathways

The detailed kinetic mechanism of ethyl valerate elaborated in this work presents good agreement with the experimental data. This mechanism is able to simulate the ethyl valerate flames at different equivalence ratios and at low pressure. From the obtained results, we present in this section the formation of species produced from ethyl valerate combustion. The main consumption pathways of ethyl valerate combustion, are also presented in this section by showing the common pathways in the three flames.

To elaborate these pathways, the calculation of the contributions is used. This calculation is performed throughout the flame and it has been presented in details in Chapter 3.

The ethyl valerate decomposition produces in the lean and stoichiometric flames, the main following species:

- EPE_{5j} (CH₂(CH₂)₃COOCH₂CH₃)
- EPE_{2j} (CH₃(CH₂)₂CHCOOCH₂CH₃)
- EPE_{3j} (CH₃CH₂CHCH₂COOCH₂CH₃)

- EPE_{4j} ($\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOCH}_2\text{CH}_3$)
- EPEM_j ($\text{CH}_3(\text{CH}_2)_3\text{COOCHCH}_3$)
- EPEE_j ($\text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2$)
- $\text{C}_4\text{H}_9\text{COOH}$

Its consumption, in the rich flame, leads to the formation of these species:

- EPE_{2j}
- EPE_{3j}
- EPE_{4j}
- EPEM_j
- $\text{C}_4\text{H}_9\text{COOH}$

4.4.1 First intermediate species

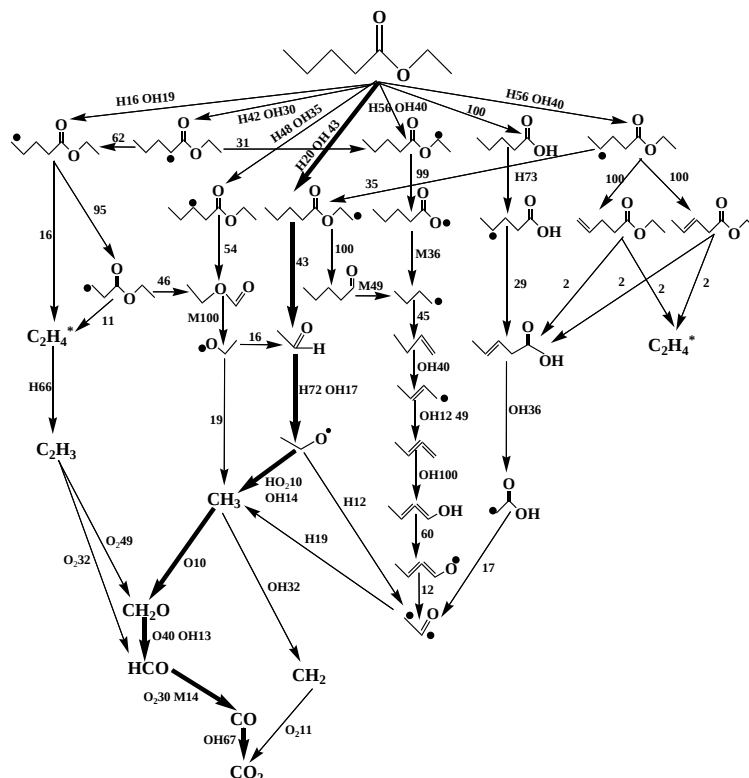
In the lean flame, the ethyl valerate is consumed by:

1. 12.5% ($\text{EPE} + \text{OH} = \text{EPEE}_j + \text{H}_2\text{O}$)
2. 10% ($\text{EPE} + \text{H} = \text{EPE}_{2j} + \text{H}_2$)
3. 10% ($\text{EPE} + \text{H} = \text{EPE}_{3j} + \text{H}_2$)
4. 10% ($\text{EPE} + \text{H} = \text{EPE}_{4j} + \text{H}_2$)
5. 9% ($\text{EPE} = \text{C}_4\text{H}_9\text{COOH} + \text{C}_2\text{H}_4$)

In the lean flame, the formation (by H abstraction) of different radicals from EPE are similar. The consumption percentage from EPE to produce those radicals are between 9 and 12.5%, as listed before.

The other first intermediate species formed from the ethyl valerate combustion with a contribution lower than 9%, reacting with H, O and OH radicals, are: EPEM_j and EPE_{5j} . These radicals are also formed from EPE_{2j} .

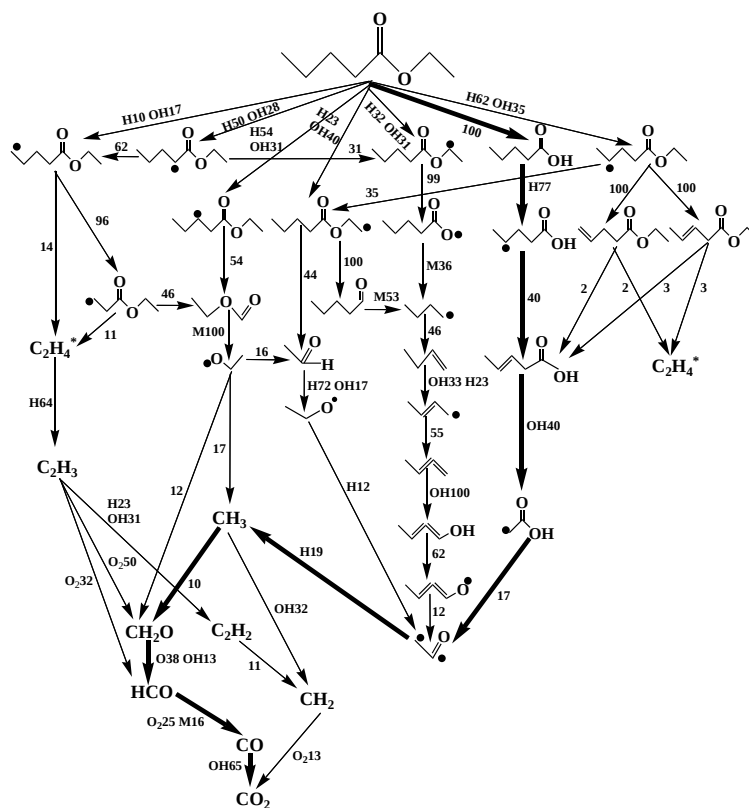
The EPEE_j formation is the "main" ethyl valerate consumption as depicted in Figure 4.24. This radical has a high BDE for its formation as shown in Figure 4.2. In the presence of oxygen, the hydrogen abstraction from CH_3 group of the ethyl radical of EPE, seems to be promoted and leads to the formation of this radical (EPEE_j).



In the stoichiometric flame, C_4H_9COOH is the main intermediate species produced from EPE consumption with a contribution of 15%:
 $EPE = C_4H_9COOH + C_2H_4$. The other first intermediate species are radicals such as: EPE_{2j} ($EPE + H = EPE_{2j} + H_2$), EPE_{3j} ($EPE + H = EPE_{3j} + H_2$), EPE_{4j} ($EPE + H = EPE_{4j} + H_2$) and $EP EEj$ ($EPE + OH = EP EEj + H_2O$), with a contribution in EPE consumption of around 11%.
 $EP EMj$ and EPE_{5j} are also formed from EPE_{2j} . These radicals are directly formed from EPE with a contribution lower than 10%.

For the rich flame, $\text{C}_4\text{H}_9\text{COOH}$ is also the main intermediate species produced from EPE consumption: 23% through ($\text{EPE}=\text{C}_4\text{H}_9\text{COOH} + \text{C}_2\text{H}_4$). EPE_{2j} , EPE_{3j} and EPE_{4j} are produced from ethyl valerate with a contribution of 12%:

- $\text{EPE} + \text{H} = \text{EPE}_2 + \text{H}_2$



- $\text{EPE} + \text{H} = \text{EPE}_{3j} + \text{H}_2$
- $\text{EPE} + \text{H} = \text{EPE}_{4j} + \text{H}_2$

Contrary to the lean flame, the main intermediate species produced from EPE is C_4H_9COOH instead of EPEEj, in the stoichiometric and rich flames. Indeed, the formation of EPEEj radical requires a BDE of 99.92 kcal/mol (Figure 4.2). This BDE is higher than 87.17 kcal/mol leading to the formation of $C_4H_9CO_2$ and C_2H_5 radicals, due to the carboxyl function. This $C_4H_9CO_2$ radical (pentanoate radical or valerate radical) reacts instantaneously with the H radical from C_2H_5 (ethyl radical) in the stoichiometric and the rich flames, to produce two stable molecules (C_2H_4 and C_4H_9COOH). The main consumption of ethyl valerate combustion leads thus to the production of valeric acid in the stoichiometric and the rich conditions.

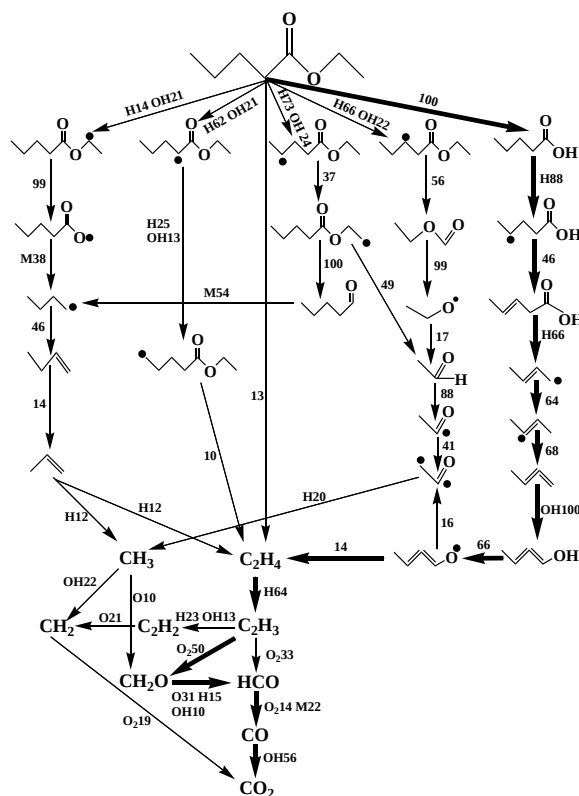


Figure 4.26: Formation reaction pathways from ethyl valerate combustion in the rich flame (thick black lines=main pathways).

From the BDE values of ethyl valerate (Figure 4.2), at high temperature and in the presence of oxygen, the H abstraction (C-H rupture) is more promoted than the carbon radical rupture (C-C rupture). The H radical, more predominant in these flames (stoichiometric and rich ones), leads to the formation of stable molecules.

Contrary to the lean and stoichiometric flames, in the rich flame, the EPEEj radical is produced from EPE_{4j} by the isomerisation reaction: EPE_{4j}=EPEEj with a contribution of 37%.

For the three flames, all first intermediate species are oxygenated compounds (radicals or stable chemical compounds), except C₂H₄.

4.4.2 Other intermediate species

In the lean flame, the main pathway of ethyl valerate consumption produces EPEEj radical by the following reactions: $\text{EPE} + \text{H} = \text{EPEEj} + \text{H}_2$ with 19% in contribution, and mainly $\text{EPE} + \text{OH} = \text{EPEEj} + \text{H}_2\text{O}$ with a contribution of 43%. The EPEEj radical leads to the production of acetaldehyde by decomposition, with a contribution of 43%: $\text{EPEEj} = \text{CH}_3\text{CHO} + \text{NC}_4\text{H}_9\text{CO}$.

The acetaldehyde is the first intermediate species analyzed experimentally, in this study. Acetaldehyde is directly produced from EPEEj and indirectly from EPE_3j , EPE_2j and EPE_5j (Figure 4.24).

The acetaldehyde, then, reacts with the H radical for 72% and OH for 17% to produce the CH_3CO radical. This radical (CH_3CO) produces methyl radical (CH_3) with a contribution of 24%. The methyl radical, the first hydrocarbon compound produced in the lean ethyl valerate flame, is also formed from other pathways:

- $\text{EPE}_3\text{j} \longrightarrow \text{C}_2\text{H}_5\text{OCO} \longrightarrow \text{CH}_3\text{CH}_2\text{O} \longrightarrow \text{CH}_3$
- $\text{C}_4\text{H}_7\text{COOH} \longrightarrow \text{CH}_2\text{COOH} \longrightarrow \text{CH}_2\text{CO} \longrightarrow \text{CH}_3$

CH_3 radical reacts with the O radical to produce formaldehyde. The formaldehyde produces HCO radical, then CO and finally CO_2 , the classical pathway of combustion.

In comparison with the lean flame, the stoichiometric and the rich flames have another main ethyl valerate consumption pathway. The main consumption of EPE is the production of valeric acid. The valeric acid produces with a contribution of 77% and 88% the $\text{BuCOOH}-4$ ($\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOH}$) radical by reacting with H radical, in the stoichiometric and the rich flames, respectively.

In the stoichiometric flame, 40% of pentenoic acid ($\text{C}_4\text{H}_7\text{COOH}$) is produced from $\text{BuCOOH}-4$ ($\text{CH}_3\text{CHCH}_2\text{CH}_2\text{COOH}$) radical. The pentenoic acid reacts with OH radical to produce CH_2COOH radical by this reaction: $\text{C}_4\text{H}_7\text{COOH} + \text{OH} = \text{CH}_2\text{COOH} + \text{C}_2\text{H}_5\text{CHO}$, with a contribution of 40%.

Then, CH_2COOH produces the CH_2CO radical that leads to the production of the methyl radical by reacting with H radical. From CH_3 radical to CO_2 , the reaction pathway is the same than in the lean flame. Some differences in the formation percentages for intermediate species appear between both ethyl

valerate flames.

The ethyl valerate consumption pathway in the rich flame is quite the same than in the stoichiometric one : from EPE to the production of pentenoic acid (C_4H_7COOH). The difference between the two flames is due to the more abundant oxygenated species concentrations in the stoichiometric flame.

In the rich ethyl valerate flame, EPE consumption leads to the hydrocarbon compounds formation (Figure 4.26). In this flame, C_4H_7-1 radical is produced from pentenoic acid with a contribution of 66% through this reaction: $C_4H_7COOH + H = C_4H_7-1 + HOCO$. The formed hydrocarbon leads to the formation of C_4H_7-3 radical (64%), then C_4H_6 (68%). The last species reacts with OH to produce HOC_4H_6 , with a contribution of 100%. Then, 66% of OC_4H_6 is produced from HOC_4H_6 as shown in the following reaction: $HOC_4H_6 \rightarrow OC_4H_6 + H$. The OC_4H_6 chemical compound leads to the formation of ethylene (C_2H_4) with a contribution of 14%. Ethylene is also formed with a contribution of 13%, 12% and 10% according to these reactions, respectively:

1. $EPE \rightarrow C_2H_4$
2. $EPEM_j \rightarrow C_4H_9CO_2 \rightarrow PC_4H_9 \rightarrow C_4H_8 \rightarrow C_3H_6 \rightarrow C_2H_4$
3. $EPE_{2j} \rightarrow EPE_{5j} \rightarrow C_2H_4$

C_2H_4 is a major hydrocarbon intermediate species analyzed, experimentally. In the rich flame, these two intermediate species, C_4H_9COOH and C_2H_4 , have been taken into account as references to validate the kinetic model.

Indeed, the consumption of ethyl valerate produces mainly these both stable chemical compounds by the reaction: $EPE = C_4H_9COOH + C_2H_4$. As the two intermediate species have been analyzed experimentally, their good profiles prediction by the model was the first validation step.

The production of the C_2H_3 radical comes from ethylene by this reaction: $C_2H_4 + H = C_2H_3 + H_2$ with a contribution of 64%. C_2H_3 produces formaldehyde with a contribution of 50% and HCO radical (33%). The HCO is mainly produced from CH_2O (56%) and leads to the formation of CO and CO_2 .

H is the main radical produced in the ethyl valerate rich flame. In the stoichiometric flame, both H and OH carry on the ethyl valerate combustion. The O radical is more abundant in the lean flame than OH and H.

4.4.3 Common ethyl valerate combustion pathways

The comparison between the main ethyl valerate consumption pathways at different equivalence ratios, in the low pressure flat flames is synthesized in this section. From Figures 4.24, 4.25 and 4.26, the main ethyl valerate consumption pathways in the three investigated flames is summarized in Figure 4.27.

In Figure 4.27, the common route in the stoichiometric and the rich flames is from ethyl valerate to pentenoic acid. From the pentenoic acid to the formation of the C_2H_3 radical via ethylene, the kinetics in the rich ethylene flame is different with the formation of hydrocarbons. In, the stoichiometric flame, the production of oxygenated species are predominant until the formation of methyl radicals.

In the lean flame, other oxygenated intermediates are produced until the methyl radical formation. In the three flames, the main ethyl valerate consumption pathway is commonly the same from formaldehyde to the carbon dioxide formation following the classical pathway of combustion.

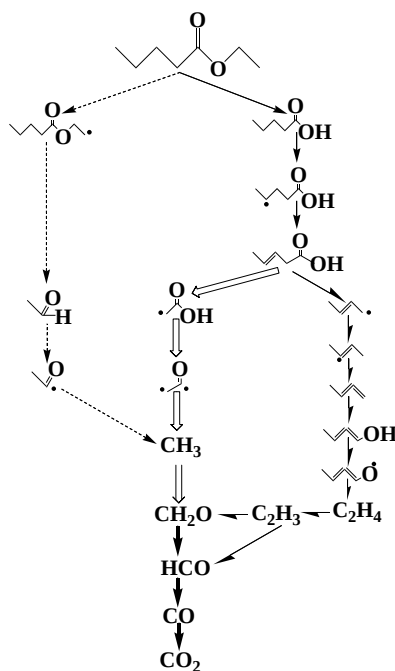


Figure 4.27: Synthetic consumption schematic pathway of ethyl valerate combustion: dotted arrow (lean flame), full arrow (stoichiometric and rich flames), full arrow with half at the tip (rich flame), large arrow (stoichiometric flame), large arrow opened at the basis (lean and stoichiometric flames) and thick black lines (lean, stoichiometric and rich flames).

4.5 Comparison between Dayma and Katshiatshia mechanisms

Dayma et al. [11] studied the ethyl valerate combustion in a jet stirred reactor at 10 atm and different equivalence ratios as explained in Chapter 1. They elaborated a kinetic mechanism that predicts with good agreement the experimental data. To test the reliability of the model at low pressure, we have simulated the rich flame with Dayma's model.

In this section, the two mechanisms are compared with ethyl valerate rich flame experimental data.

The mechanism predicts with good agreement the mole fraction profiles of the main species such as: the fuel (Figure 4.28), the oxidizer (Figure 4.29) and the products (CO , CO_2 , H_2O and H_2 : Figures 4.30 - 4.33).

However, for the intermediate species, the simulation overestimates the experimental data of $\text{C}_4\text{H}_9\text{COOH}$ (Figure 4.34), CH_3CHO (Figure 4.35), C_2H_4 (Figure 4.39) and CH_4 (Figure 4.40). For acetone (Figure 4.38) and formic acid (Figure 4.37), Dayma's mechanism underestimates the experimental mole fraction profiles. Finally, this mechanism presents a good agreement with the experimental data for formaldehyde (Figure 4.36) and acetylene (Figure 4.41).

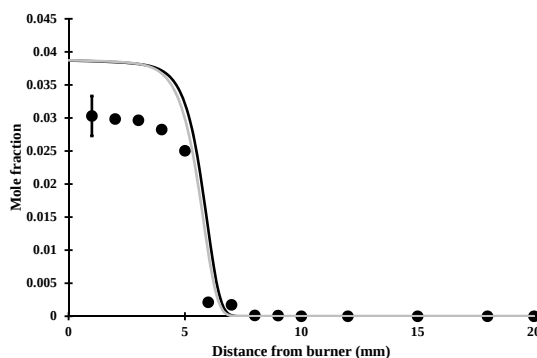


Figure 4.28: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) EPE mole fraction profiles for rich ethyl valerate flame.

In regards of all the results carried out, the first intermediate species in the ethyl valerate combustion at high and low pressures are the same: EPE_5j , EPE_4j , EPE_3j , EPE_2j , EPEEj , EPEMj , $\text{C}_4\text{H}_9\text{COOH}$ and C_2H_4 .

At high temperature and pressure, O_2 reacts with the ethyl valerate to form

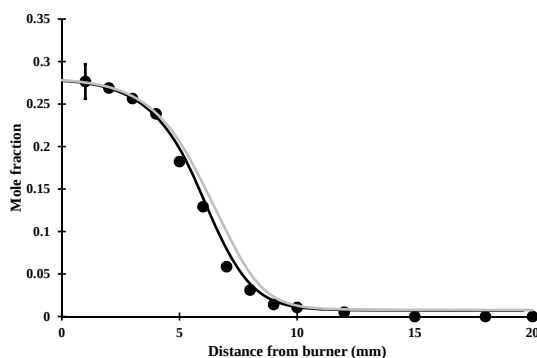


Figure 4.29: Experimental (symbols) and Simulated (solid lines): black (Katshiathia mechanism) and grey (Dayma mechanism) O_2 mole fraction profiles for rich ethyl valerate flame.

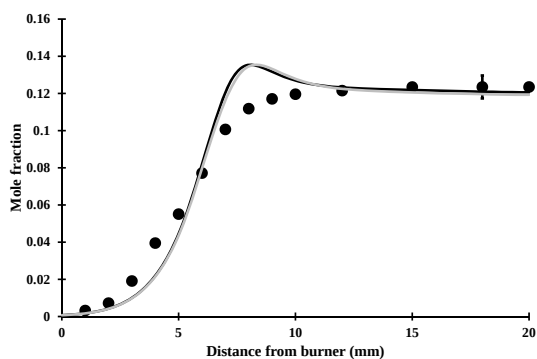


Figure 4.30: Experimental (symbols) and Simulated (solid lines): black (Katshiathia mechanism) and grey (Dayma mechanism) CO mole fraction profiles for rich ethyl valerate flame.

species containing more than 2 oxygen atoms. When the temperature decreases, this effect is reduced. At low pressure, H, OH and O are the most important radicals in the ethyl valerate combustion, and the EPE consumption does not lead to the formation of intermediate species with more than 2 oxygen atoms. The Katshiathia mechanism allows to improve the simulation of intermediate species produced from the ethyl valerate combustion at low pressure.

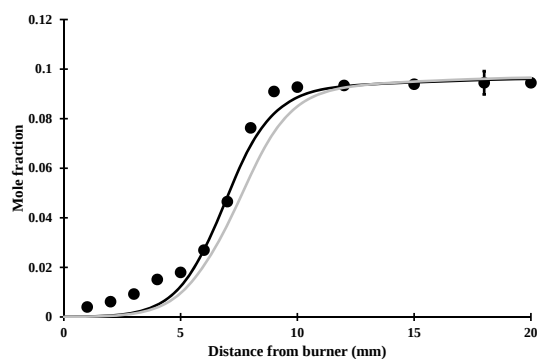


Figure 4.31: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) CO₂ mole fraction profiles for rich ethyl valerate flame.

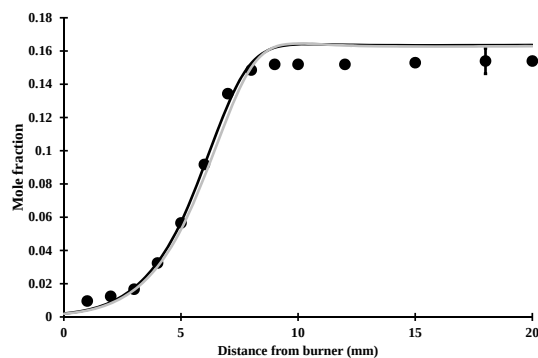


Figure 4.32: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) H₂O mole fraction profiles for rich ethyl valerate flame.

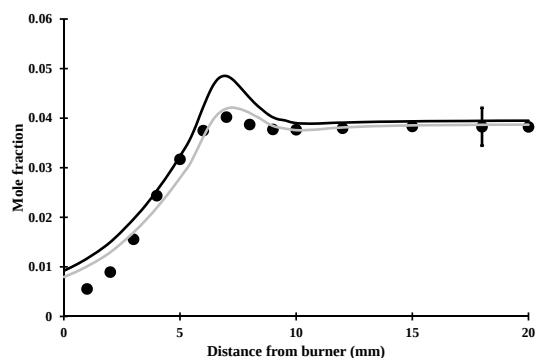


Figure 4.33: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) H₂ mole fraction profiles for rich ethyl valerate flame.

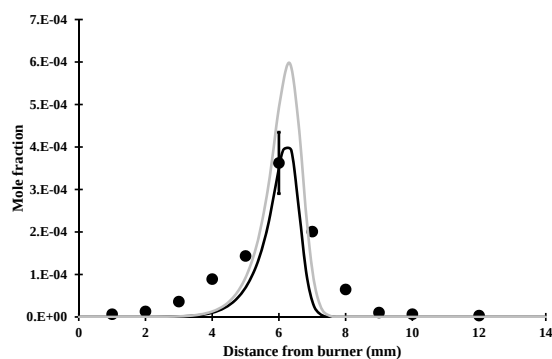


Figure 4.34: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) C_4H_9COOH mole fraction profiles for rich ethyl valerate flame.

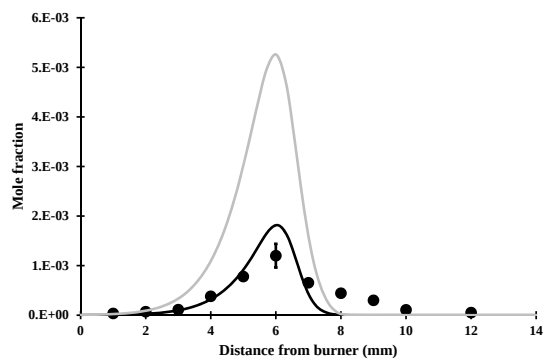


Figure 4.35: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) CH_3CHO mole fraction profiles for rich ethyl valerate flame.

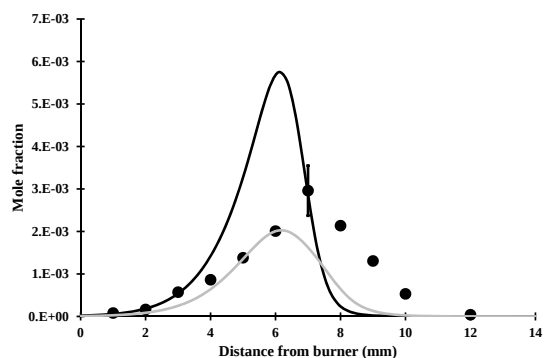


Figure 4.36: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) CH_2O mole fraction profiles for rich ethyl valerate flame.

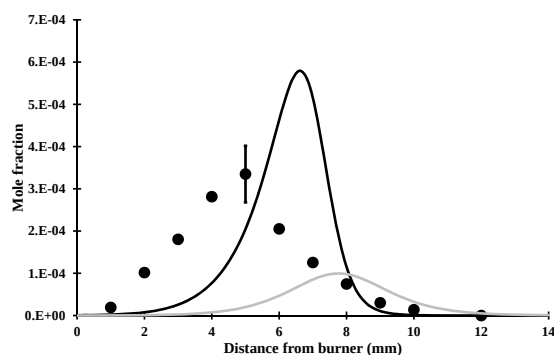


Figure 4.37: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) HOCHO mole fraction profiles for rich ethyl valerate flame.

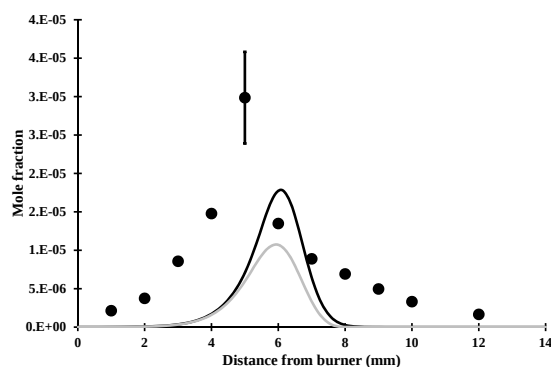


Figure 4.38: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) CH_3COCH_3 mole fraction profiles for rich ethyl valerate flame.

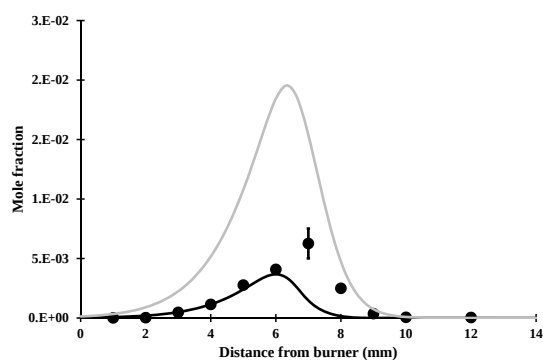


Figure 4.39: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) C_2H_4 mole fraction profiles for rich ethyl valerate flame.

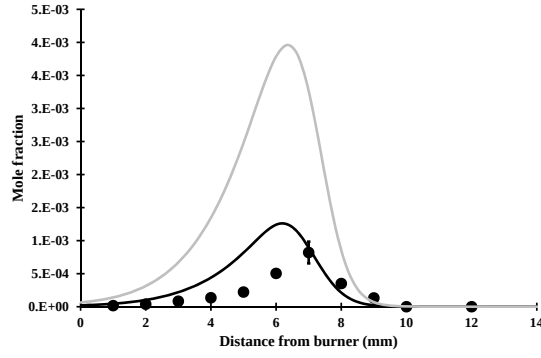


Figure 4.40: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) CH_4 mole fraction profiles for rich ethyl valerate flame.

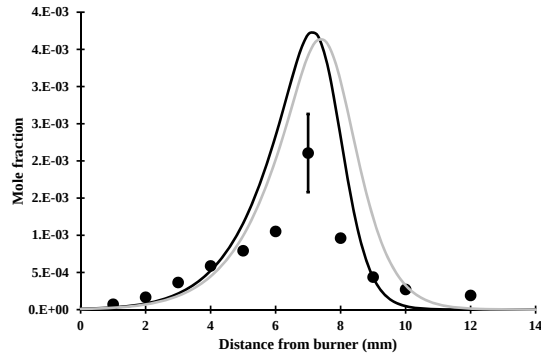


Figure 4.41: Experimental (symbols) and Simulated (solid lines): black (Katshiatshia mechanism) and grey (Dayma mechanism) C_2H_2 mole fraction profiles for rich ethyl valerate flame.

4.6 Validation of Katshiatshia mechanism at high pressure

The Katshiatshia mechanism has been tested by Guillaume Dayma in a jet-stirred reactor to check its reliability at high pressure (10 atm) in stoichiometric conditions described in their studies on ethyl valerate combustion [11]. In Figure 4.42, the simulated mole fraction profiles of EPE ($C_7H_{14}O_2$) and methane (CH_4) agree very well with the experimental ones. For ethylene, the agreement between the experimental mole fraction profile and the simulated is quite good (Figure 4.42), even if this species is slightly underestimated by the model. In the same figure, the H_2 simulated concentration profile is underestimated compared to the experimental one. For the three main products, CO, CO_2

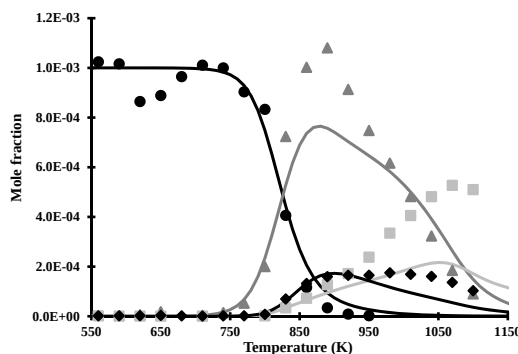


Figure 4.42: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of EPE (black circles), C_2H_4 (grey triangles), H_2 (light grey squares) and CH_4 (black diamonds) in a jet-stirred reactor.

and H_2O , the agreement between the simulated mole fraction profiles and the experimental ones is very good (Figure 4.43). Based on the results presented in Figure 4.44, the O_2 simulated mole fraction profile agrees very well with the experimental one. For the intermediate species such as valeric acid, propene, butadiene, formaldehyde and acetaldehyde (Figures 4.45 - 4.47), the model predicts very well the experimental concentrations. In Figure 4.47, the simulated mole fraction profile of acetylene (C_2H_2) underestimates the experimental one.

Based on the results presented in this section, the Katshiatshia mechanism predicts with a good agreement the experimental mole fraction profiles at high pressure for species such as : $C_7H_{14}O_2$, O_2 , CO, CO_2 , H_2O , C_4H_9COOH , C_2H_4 , CH_2O and CH_3CHO . However, the present kinetic model is not able to predict correctly the experimental mole fraction profiles of H_2 and C_2H_2 , in

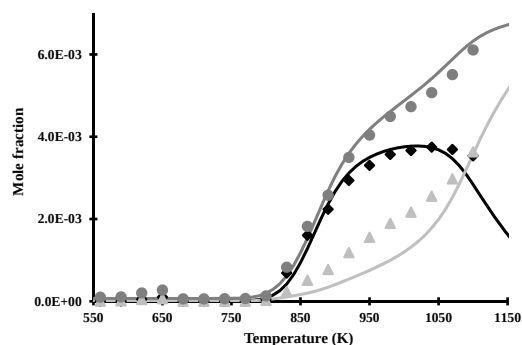


Figure 4.43: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of H_2O (grey circles), CO (black diamonds) and CO_2 (light grey triangles) in a jet-stirred reactor.

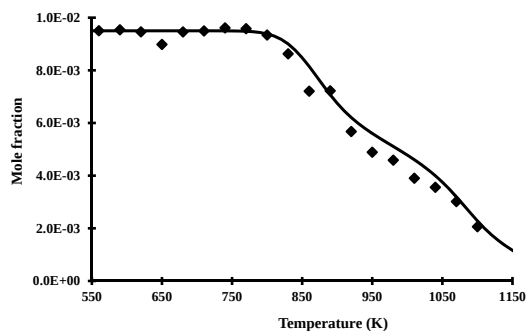


Figure 4.44: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of O_2 in a jet-stirred reactor.

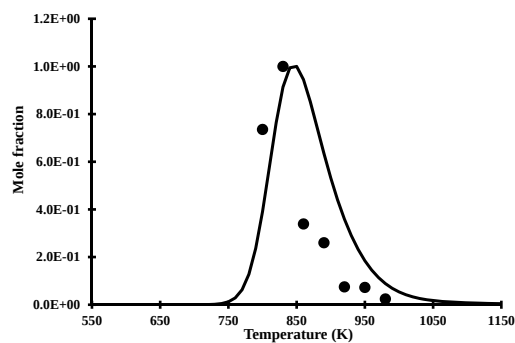


Figure 4.45: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of $\text{C}_4\text{H}_9\text{COOH}$ in a jet-stirred reactor.

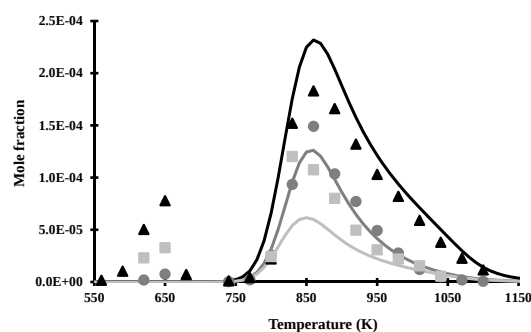


Figure 4.46: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of CH_2O (black triangles), CH_3CHO (light grey squares) and C_3H_6 (grey circles) in a jet-stirred reactor.

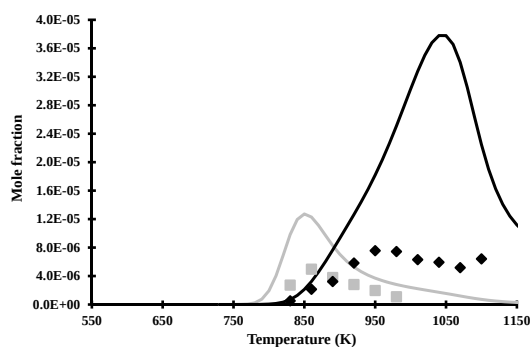


Figure 4.47: Experimental (symbols) and Simulated (solid lines) mole fraction profiles of C_2H_2 (black diamonds) and $i\text{-C}_4\text{H}_6$ (light grey squares) in a jet-stirred reactor.

these conditions.

4.7 Ethyl valerate laminar burning velocities

The combustion behaviour of fuels can be understood by the determination of parameters such as the ignition delay, the species distribution during the combustion, the flame propagation speed and the energy released [114]. These parameters can be determined by the chemical kinetic model of the fuel. A good prediction of these parameters is crucial to use the mechanisms in industrial processes (engines, boilers, furnaces, ...) to define the best operating conditions.

The laminar burning velocity is one of these fundamental properties and its reliable prediction is essential for combustion applications [115].

In the present section, the ethyl valerate laminar burning velocities are presented by comparing the simulated results obtained from the mechanism elaborated in this study to the experimental data from Lund University determined by Elna J.K. Nilsson [116]. Moreover, the comparison between these results and Dayma mechanism are also presented.

The laminar burning velocities of ethyl valerate were determined, experimentally, at Lund University using a heat flux setup as described by Nauc  r et al. [117]. Elna J.K. Nilsson [116] performed the experiments at atmospheric pressure and different equivalence ratios ($\phi = 0.7$ to 1.2) with initial gas mixture temperatures of 318, 328 and 338 K.

The method used by the authors to determine the heat flux of ethyl valerate laminar burning velocities was developed by P. de Goey [118]. This method developed for gaseous mixtures, has been adapted for the determination of the laminar burning velocities of liquid fuels [119].

Figure 4.48 illustrates the ethyl valerate laminar burning velocities. In Figure 4.48, the kinetic mechanism, elaborated and validated against ethyl valerate flat flames at low pressure, overestimates the experimental data proposed by Elna J.K. Nilsson [116]. However, the Dayma's ethyl valerate mechanism predicts with a good agreement the experimental data. It should be noticed that this latter mechanism was elaborated and validated against experimental data at atmospheric and high pressure.

To improve our detailed kinetic mechanism, a literature review on laminar burning velocities has been performed. We underline the influence of the parameters used in the softwares, on the flame velocities (Figure 4.48). With Chemkin II [120] the flame speed is 77.0 cm/s at equivalence ratio 1.1, and

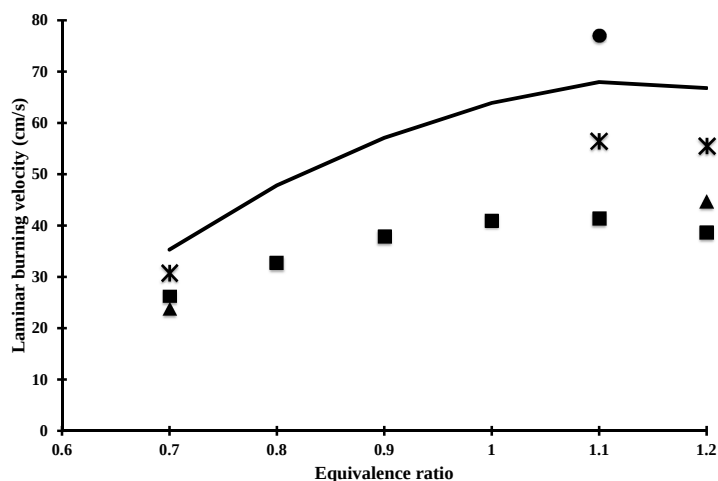


Figure 4.48: Ethyl valerate laminar burning velocities at 328 K: lines (Katshiatschia mechanism by OpenSMOKE), circles (Katshiatschia mechanism by Chemkin II), stars (Katshiatschia modified mechanism by OpenSMOKE), triangles (Dayma mechanism [11]) and squares (experimental data [116]).

67.97 cm/s with OpenSMOKE [121], using the Katshiatschia model.

To reduce the discrepancy between our mechanism and the experimental data, we tried to validate the UCL model [111] with the methane and the ethylene experimental flame speeds proposed by Gu et al. [122] and Park et al. [123], respectively. The UCL mechanism is a part of Katshiatschia mechanism from C_4 to H_2/O_2 system. As Dayma mechanism predicts well the ethyl valerate laminar burning velocities at atmospheric pressure, we checked the validity of UCL mechanism at the same conditions.

In Figures 4.49 and 4.50, the UCL mechanism overestimates the laminar burning velocities of methane and ethylene at atmospheric pressure. Due to this effect, four elementary chemical reactions from the literature have been identified as very sensitive to the pressure in flame speed calculations [11, 124, 125, 126]. Table 4.8 shows the four pressure sensitive elementary chemical reactions. Due to these modifications in the UCL mechanism, the new detailed kinetic mechanism is called "modified UCL mechanism". This improved kinetic mechanism agrees very well with experimental data for methane and ethylene laminar burning velocities (Figures 4.49 and 4.50) proposed by Gu et al. [122] and Park and al. [123], respectively.

Based on these results, we replace these four elementary chemical reactions in Katshiatschia mechanism to check its validity for ethyl valerate experimental

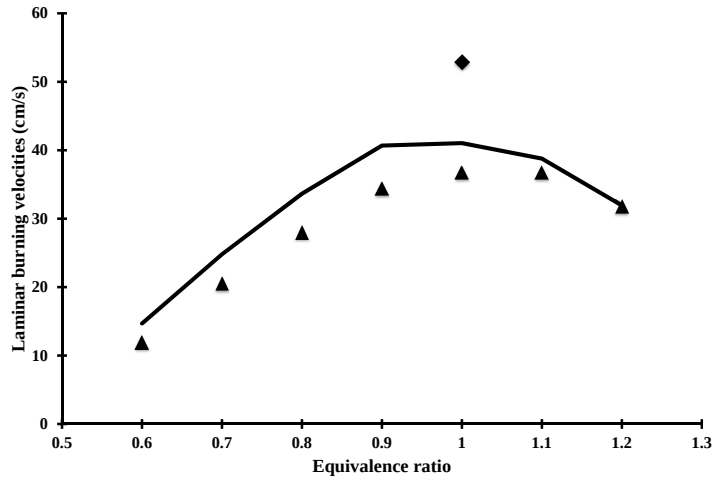


Figure 4.49: Methane laminar burning velocities: lines (modified UCL mechanism), diamonds (UCL mechanism), triangles (Gu et al. experimental data [122]).

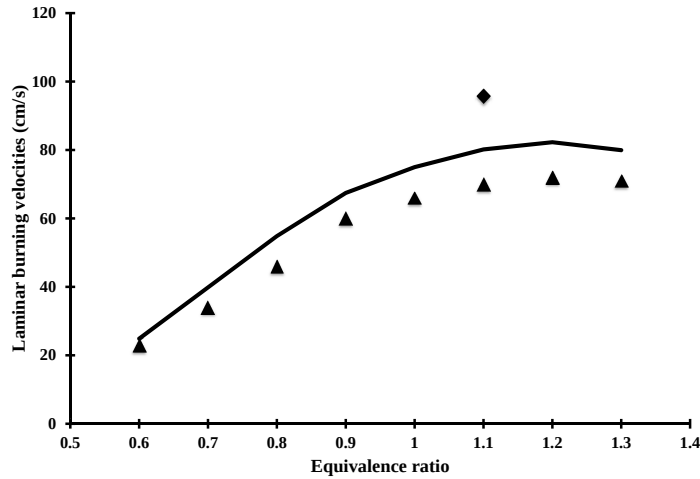


Figure 4.50: Ethylene laminar burning velocities: lines (modified UCL mechanism), diamonds (UCL mechanism), triangles (Park et al. experimental data [123]).

laminar burning velocities data. The obtained mechanism is called : "Katshiatshia modified mechanism". These modifications allow to reduce the simulated values of ethyl valerate laminar burning velocities from 35.3 to 30.69 cm/s at $\phi = 0.7$; from 67.97 to 56.5 cm/s at $\phi = 1.1$ and, finally, from 66.8 to 55.4 cm/s at $\phi = 1.2$. These results are also plotted in Figure 4.48.

Table 4.8: Rate constant modifications performed to improve laminar burning velocities prediction.

Mechanism	Reaction	A $cm^3 mol^{-1} s^{-1}$	n	Ea $cal/mole$	Ref
1. UCL	$HCO + M = H + CO + M$	4.75E+11	0.66	1.487E+04	[65, 111]
UCL modified	$HCO + M = H + CO + M$	1.87E+17	-1.0	1.700E+04	[112]
2. UCL	$CH_3 + H + M = CH_4 + M$	8.00E+26	-3.0	0.000E+00	[65, 111]
UCL modified	$CH_3 + H + M = CH_4 + M$	1.20E+15	-0.4	0.000E+00	[124]
3. UCL	$CH_2O + M = HCO + H + M$	3.30E+39	-6.3	9.9904E+04	[65, 111]
UCL modified	$CH_2O + M = HCO + H + M$	1.826E+32	-4.42	8.712E+04	[11]
	REV	5.070E+27	-3.42	8.435E+04	[11]
4. UCL	$CH_3 + OH = CH_2(S) + H_2O$	3.61E+03	0.0	0.000E+00	[65, 111]
UCL modified	$CH_3 + OH = CH_2(S) + H_2O$	6.37E+18	-1.67	1.1141E+04	[127]

4.8 Comparison between the two mechanisms on ethyl valerate flat flames

After the improvement of the model for laminar burning velocities, we propose to compare the two mechanisms (Katshiatshia and modified Katshiatshia) on the ethyl valerate flat flames studied at low pressure. Figures 4.51 - 4.64 show the comparison between the simulated mole fraction profiles of all the species analyzed in this work in the rich ethyl valerate flame.

The fuel (EPE), the oxidizer (O_2) and the main products such as CO , CO_2 , H_2O and H_2 have the same mole fraction profiles with the two kinetic mechanisms (Figures 4.51 - 4.56).

Katshiatshia modified mechanism overestimates the valeric acid concentration by a factor of 2.25 in the rich ethyl valerate valerate (Figure 4.57). This overestimation is due to the change of the four elementary reactions as presented previously. The C_4H_9COOH consumption is reduced by the co-reactants concentrations influenced by these 4 reactions. It should be noted that the Katshiatshia mechanism agrees very well with the valeric acid experimental mole fraction profile. The two mechanisms present a good agreement for ethylene concentrations in the rich ethyl valerate flame compared to the experimental mole fraction profile (Figure 4.58). Acetaldehyde, formaldehyde and methane simulated mole fraction profiles agree well with the experimental

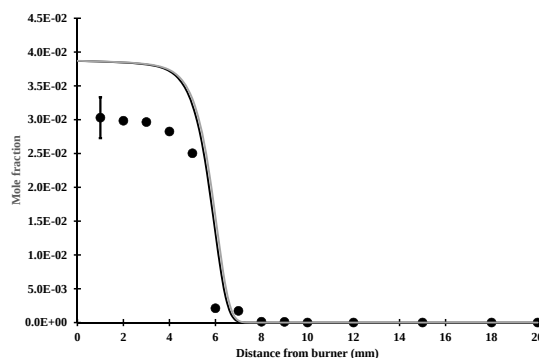


Figure 4.51: Mole fraction profiles of ethyl valerate in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

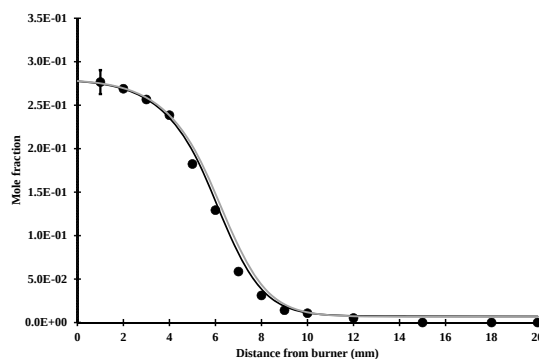


Figure 4.52: Mole fraction profiles of oxygen in rich ethyl valerate: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

mole fraction profiles for both ethyl valerate mechanisms (Figures 4.59, 4.60 and 4.61).

Acetylene and formic acid are slightly overestimated by the Katshiatshia modified mechanism compared to the Katshiatshia one (Figures 4.62 and 4.63). However, both mechanisms predict with a good agreement the experimental mole fraction profiles of these species. For acetone (Figure 4.64), both mechanisms underestimate the experimental acetone mole fraction profile. However, these discrepancies are not very significant due to the low concentrations of CH_3COCH_3 .

Globally, for all the species, the two mechanisms present the same simulated mole fraction profiles, except for the valeric acid.

4.8. Comparison between the two mechanisms on ethyl valerate flat flames133

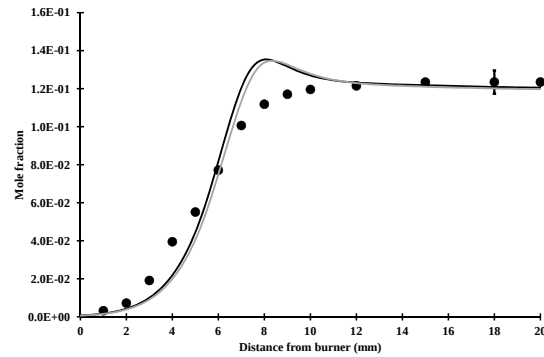


Figure 4.53: Mole fraction profiles of carbon monoxide in rich ethyl valerate: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

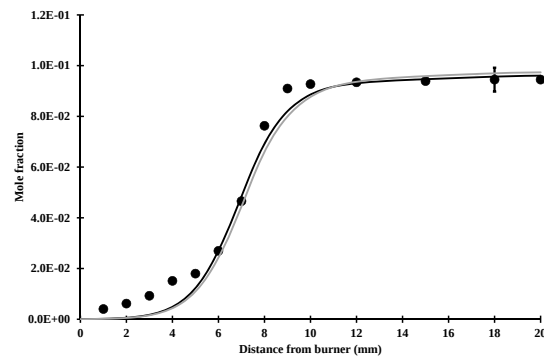


Figure 4.54: Mole fraction profiles of carbon dioxide in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

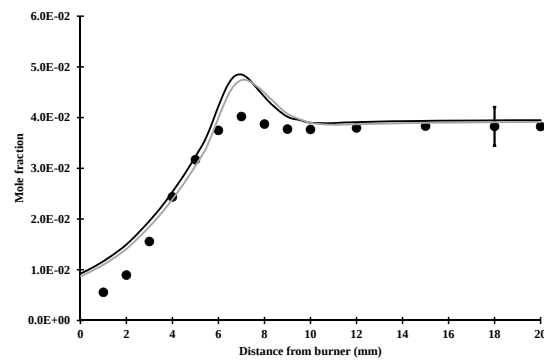


Figure 4.55: Mole fraction profiles of hydrogen in rich ethyl valerate: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

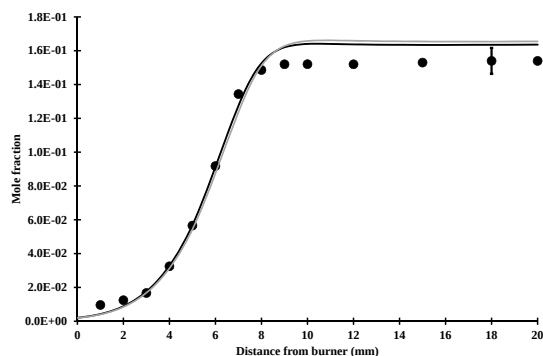


Figure 4.56: Mole fraction profiles of water in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

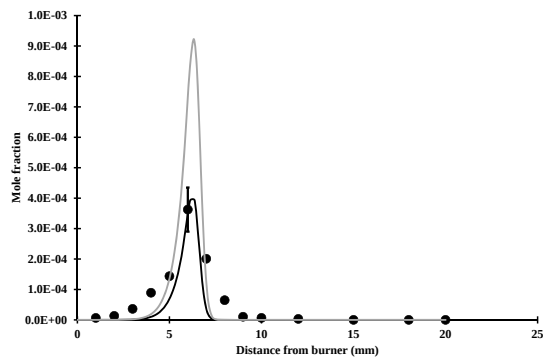


Figure 4.57: Mole fraction profiles of valeric acid in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

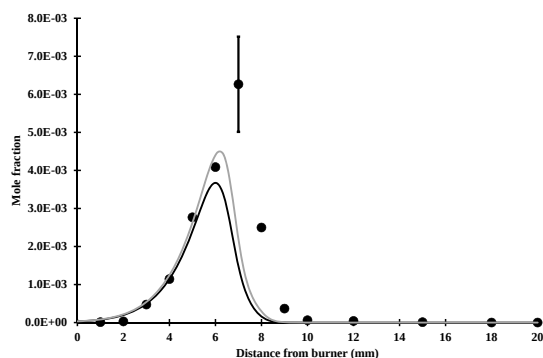


Figure 4.58: Mole fraction profiles of ethylene in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

4.8. Comparison between the two mechanisms on ethyl valerate flat flames¹³⁵

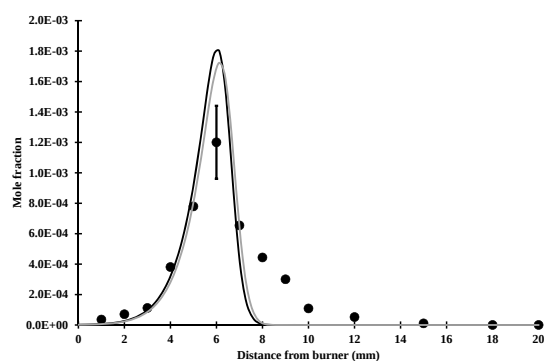


Figure 4.59: Mole fraction profiles of acetaldehyde in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

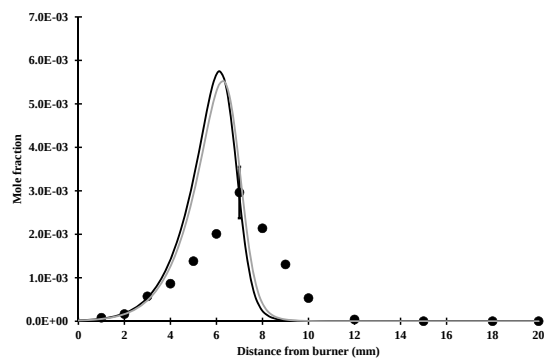


Figure 4.60: Mole fraction profiles of formaldehyde in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

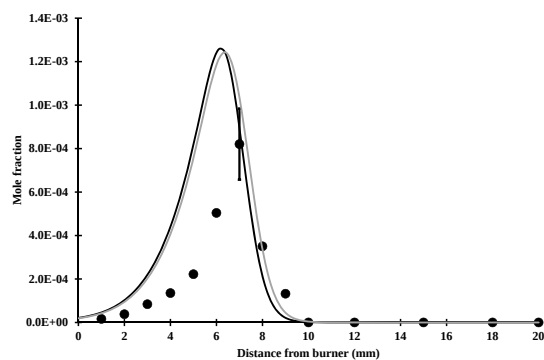


Figure 4.61: Mole fraction profiles of methane in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

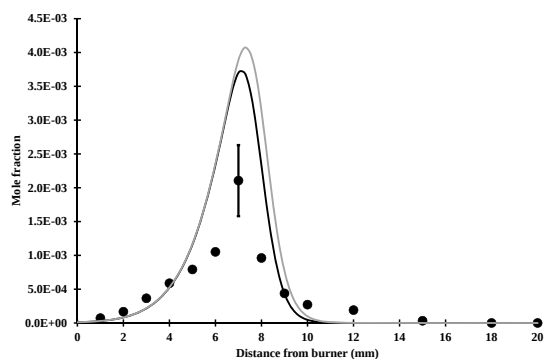


Figure 4.62: Mole fraction profiles of acetylene in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

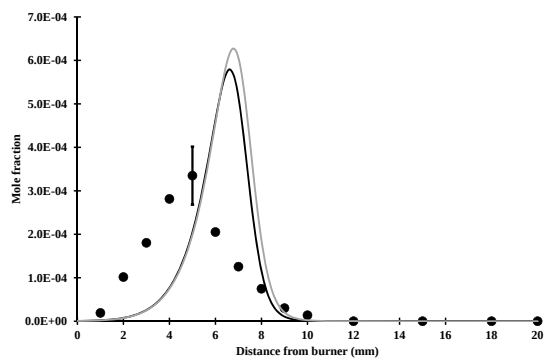


Figure 4.63: Mole fraction profiles of formic acid in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

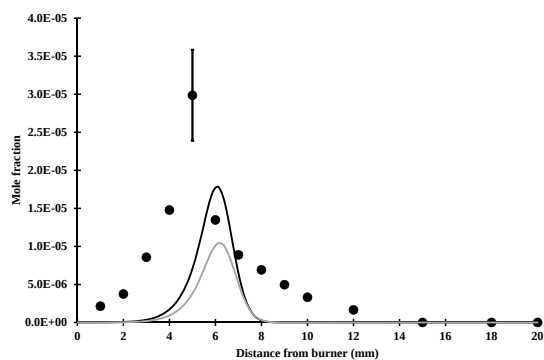


Figure 4.64: Mole fraction profiles of acetone in rich ethyl valerate flame: black line (Katshiatshia mechanism) and grey line (Katshiatshia modified mechanism) and circles (experimental data).

Conclusion

The detailed kinetic model was elaborated and optimized from UCL and Dayma mechanisms. The new detailed kinetic model is able to predict the ethyl valerate combustion at low pressure. The concentration of main species such as EPE, O_2 , Ar, CO, CO_2 , H_2 and H_2O present a very good agreement between the simulated and experimental profiles. The oxygenated species are the important intermediate species in the ethyl combustion and there is a good agreement between the simulated and experimental concentration profiles. The valeric acid (C_4H_9COOH), is a very reactive molecule but the simulated and experimental mole fraction profiles present a very good agreement in the rich flame, and a good agreement in the lean flame. In the stoichiometric flame, the simulated mole fractions are overestimated. The concentrations of hydrocarbon compounds such as C_2H_4 and CH_4 are well simulated in the three flames. C_2H_2 is only detected and measured in the rich flame, and the experimental mole fraction profile presents a good agreement with the simulated one.

Generally, the equivalence ratio effect is well observed for all the investigated species in the three ethyl valerate, except for the valeric acid.

From the results obtained numerically, we can validate the new kinetic model for the ethyl valerate combustion at low pressure at these equivalence ratios. Thanks to this mechanism, the ethyl valerate consumption pathways were established from the fuel to the carbon dioxide.

However, the new detailed kinetic mechanism (Katshiatshia mechanism) elaborated in this work, overestimated the experimental ethyl valerate laminar burning velocities data. To improve the elaborated mechanism, the UCL model (part of this mechanism) was tested against methane and ethylene experimental laminar burning velocities data at atmospheric pressure. This mechanism overestimated these experimental data and four reactions were found to be very sensitive with the pressure. The modification of these four elementary chemical reactions improves the agreement between the simulations with this modified UCL model and experimental data for the methane and ethylene laminar burning velocities.

The improvement of the complete model (Katshiatshia modified mechanism) allows to decrease, significantly, the ethyl valerate flame speed values at atmospheric pressure. To extend its reliability at high pressure (10 atm), the Katshiatshia mechanism has been tested against experimental data obtained in a jet-stirred reactor at stoichiometric condition. The mechanism agrees well,

generally, with these experimental data.

However, the two mechanisms (Katshiatshia and Katshiatshia modified mechanisms) present the same simulated mole fraction profiles for all species except for the valeric acid. The modification of these four reactions reduces the valeric acid consumption leading to an overestimation of its concentration.

General conclusions and perspectives

Biofuels are used to rely on more abundant and sustainable supply chains than traditional fuels such as gasoline and gasoil. Biomass can produce liquid biofuels by processing lignocellulosic materials. Levulinic acid formed from lignocellulose via two-step hydrogenation reactions, can then generate valeric esters via an esterification reaction. These valeric esters are methyl, ethyl, propyl, butyl and pentyl valerate. Due to their physicochemical properties, the first three molecules could be used in replacement of gasoline in spark ignition engines, the last two could be used in compression ignition engines in replacement of gasoil. Due to their potential automotive applications, these valeric esters have to be characterized by a study of their combustion mode at high pressure. To elaborate detailed kinetic mechanisms of these fuels, the experimental studies at high pressure must be combined with those at low pressure.

This study focused on ethyl valerate in order to characterize its combustion at low pressure by analyzing premixed one dimensional flat flames at three equivalence ratios (rich, stoichiometric and lean). Dayma et al. [11] characterized ethyl valerate combustion at high pressure (10 *atm*) in a jet stirred reactor and its laminar burning velocities in a range of pressures (1, 3 and 5 *atm*) and at 423 *K*. No results exist at low pressure. The characterization of a fuel combustion at low pressure, is necessary because all intermediate species can be determined experimentally and then used for the elaboration of a detailed kinetic model. This mechanism will be able to predict the formation of different pollutants such as hydrocarbon compounds (soot precursors) and oxygenated species (aldehyde).

To reach this objective, an existing test bench was improved to allow combustion of heavier chemical compounds. This experimental setup contains an

evaporation system for species with high boiling point. The evaporated fuel, mixed with argon as a vector gas, is then blended with the oxidizer to have premixed conditions. To avoid condensation of the premixed gas, heated ribbons are used at each cool part and piping junction before the combustion chamber. In the combustion chamber, ethyl valerate flames are stabilized on a movable burner with a surface perpendicular to a sampling quartz nozzle. As flames are stabilized at low pressure (55 *mbar*), a compression system is used to increase the pressure of the sampled gas before its injection into the gas chromatography. However, some species condense is due to the expansion after the compression. To reduce this effect, a heated ribbon is used around the compression system.

With all these modifications, the present test bench can be used in the study of liquid biofuels with high boiling points such as esters.

Three ethyl valerate flat flames at different equivalence ratios ($\phi = 0.81, 0.95$ and 1.31) were studied experimentally. The gas chromatography allows to separate and identify the fuel ($C_7H_{14}O_2$), the oxidizer (O_2), the diluent (Ar), the intermediate species such as: C_4H_9COOH , CH_3CHO , CH_2O , CH_3COCH_3 , $HOCHO$, C_2H_4 , CH_4 and C_2H_2 , and the products: CO , CO_2 , H_2O and H_2 . After calibration, the conversion of the GC's signals of these stable chemical compounds into mole fractions is performed.

A new detailed kinetic model containing 1368 elementary chemical reactions and 211 species is elaborated from Dayma and UCL mechanisms. This new kinetic model predicts with good agreement the ethyl valerate combustion at low pressure compared to the experimental data.

Based on the numerical results, the ethyl valerate main consumption pathways are elaborated. In the stoichiometric and the rich flames, the ethyl valerate consumption pathways are similar until the formation of valeric acid. Then, in the rich flame, the main ethyl valerate consumption is: $EPE \rightarrow C_4H_9COOH \rightarrow CH_3CHCH_2CH_2COOH \rightarrow CH_3CHCHCH_2COOH \rightarrow CH_3CHCHCH_2 \rightarrow CH_3CCHCH_3 \rightarrow CH_3CHCCH_2 \rightarrow CH_3CHCCOH \rightarrow CH_3CHCCO \rightarrow C_2H_4 \rightarrow C_2H_3 \rightarrow CH_2O$ and HCO . In the stoichiometric flame, the ethyl valerate combustion mainly leads to the formation of: $EPE \rightarrow C_4H_9COOH \rightarrow CH_3CHCH_2CH_2COOH \rightarrow CH_2COOH \rightarrow CH_2CO \rightarrow CH_3 \rightarrow CH_2O$ and HCO . And in the lean flame, the ethyl valerate consumption pathway is different. The radical $EPEEj$ ($CH_3(CH_2)_3COOCH_2CH_2$) produced from the main ethyl valerate consumption pathway leads to the acetaldehyde formation:

$\text{EPE} \longrightarrow \text{CH}_3(\text{CH}_2)_3\text{COOCH}_2\text{CH}_2 \longrightarrow \text{CH}_3\text{CHO} \longrightarrow \text{CH}_3\text{CO} \longrightarrow \text{CH}_3 \longrightarrow \text{CH}_2\text{O}$ and HCO . From HCO radical to CO_2 formation, the three ethyl valerate flames have the same consumption pathway as in a classical combustion.

To validate the new kinetic mechanism at atmospheric pressure, experimental ethyl valerate laminar burning velocities data obtained at 328 K were used. The simulated values overestimated the experimental data. Four reactions have been identified as sensitive to the pressure in the UCL model part of the elaborated mechanism. Their modifications allowed to validate the modified UCL mechanism for the methane and ethylene laminar burning velocities data proposed in the literature. Therefore, these modifications have been introduced in the Katshiatshia mechanism to check its validity at atmospheric pressure. The simulated values observed for these calculations, at atmospheric pressure and 328 K , have been compared to the experimental data from Lund University. The obtained Katshiatshia mechanism presents an improvement for the ethyl valerate laminar burning velocities even if the present values still overestimate the ethyl valerate experimental flame speed values.

Then, the Katshiatshia mechanism was tested and validated with the experimental data proposed by Dayma et al. [11] in a jet-stirred reactor at high pressure in stoichiometric conditions. This mechanism predicts well the experimental mole fraction profiles for the studied species except for H_2 and C_2H_2 .

Regarding automotive applications, a substitution to gasoline is possible as well as blends in different proportions. However, the experimental results show that ethyl valerate could produce two major pollutants typical to oxygenated species, acetaldehyde (0.2% in the three investigated flames) and formaldehyde (0.3% in the three studied flames). A second drawback is its chemical reactivity in the presence of oxygen that could be a disadvantage for its long term storage.

In perspectives, the characterization of ethyl valerate flat flames at low pressure using a molecular beam mass spectroscopy (MBMS) is necessary in order to further improve this new detailed mechanism. Indeed, in these experimental conditions, radicals and other stable intermediate species such as propene (C_3H_6), butadiene (C_4H_6) and pentenoic acid ($\text{C}_4\text{H}_7\text{COOH}$) not detected in gas chromatography could be measured to improve the elaborated mechanism.

Methyl valerate ($C_6H_{12}O_2$) can be produced as ethyl valerate and presents similar physico-chemical properties. Thanks to the experimental setup, this molecule could be studied experimentally. Methyl valerate has a boiling point of 126°C at atmospheric pressure. Compared to ethyl valerate, this valerate ester would be even easier to evaporate using the same setup.

Triacetine ($C_9H_{14}O_2$) is the smallest triester produced from glycerol and acetic acid, and has a boiling point of 259°C at atmospheric pressure. Due to its high boiling point, this ester presents more challenges to be evaporated in the conditions used in the present work. For this reason, if the premixed conditions could not be achieved using this molecule, hydrogen could be added. Triacetine is very important to be studied as a fuel due to its production from glycerol. Glycerol is considered as a co-product of several industrial processes and this molecule can be valued by using it in the production of biofuels such as triacetine.

Finally, the new detailed kinetic model has to be validated at atmospheric and high pressures to extend its reliability. High pressure condition is very important in connection with the industrial applications. Moreover, the Katshiatshia mechanism will be leveraged in other combustion modelling efforts. In particular, the mechanism will be coupled to Computational Fluid Dynamics (CFD) tools in order to study the performance of esters within an Homogeneous Charge Compression Ignition (HCCI) engine. To decrease the simulation time while performing calculations, it will be necessary to reduce the kinetic mechanism. This mechanism will have to achieve a delicate balance between a high level of fidelity (thus involving a large number of species) and the CFD cost (thus proportional to the number of species).

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Appendix A

Mathematical description of flames

A mathematical description of one-dimensional laminar flames using the conservation properties of mass, momentum, energy and chemical species through the flame is presented in this chapter [84].

A.1 General form of 3 dimensional conservation equations

Considering a three dimensional element α with a volume V and a surface S , the value of an extensive variable F of this 3D element as a function of time t , can be determined using the integration of its density $\rho_F(\vec{r}, t) = dF/dV$ over the volume V . Equation (A.1) in which $\vec{r}$ is a vector representing the spatial location, described this calculation:

$$F(t) = \int_V \rho_F(\vec{r}, t) dV \quad (\text{A.1})$$

Where the vector $\vec{r}$ represents the spatial location in the volume. A temporal modification of $F(t)$ can have different origins such as :

1. considering that the 3D element is located in a flux. This flux can modified the variable $F(t)$. This modification can bring or take $F(t)$ away of the volume V . Therefore this change of $F(t)$ can be due to the flux $\vec{\phi}_F \vec{n} dS$ crossing the surface S of the 3D element. $\vec{n}$ is a perpendicular

vector to the surface and $\vec{\phi}_F$ described the amount F that flows per unit of time through the surface S . Pratically, this flux can found its origin in the thermal conduction, convection, molecular diffusion phenomena, etc.

2. F can be produced or consumed in the same element. Therefore, a change in the production or consumption q_F of F in the volume V can be observed. The term q_F represents the amount of F produced or consumed per units of time and volume. This phenomenon can be a consequence of a chemical reaction.
3. a change of the term F can be described by its distant interaction with the surroundings. This change can be due to the radiation, gravity etc. The generated amount of $F(t)$ per unit of volume is p_F .

From these three consideration, an overall balance Equation (A.2) can be used to describe these phenomena:

$$\int_V \frac{\partial \rho F}{\partial t} dV + \int_S \vec{\phi}_F \vec{n} dS = \int_V q_F dV + \int_V p_F dV \quad (\text{A.2})$$

In this equation, the temporal variation of F contained in V has been written in Equation (A.3) according to Equation (A.1):

$$\frac{\partial F}{\partial t} = \int_V \frac{\partial \rho F}{\partial t} dV \quad (\text{A.3})$$

In Equation (A.2), the integration representing the change of flux $\vec{\phi}_F \vec{n} dS$ through the surface S can be converted into a volume integral using the Gauss theorem. This mathematical operation is presented in Equation (A.4) where $\vec{\nabla} \cdot \vec{\phi}_F dV$ represents the divergence.

$$\int_S \vec{\phi}_F \vec{n} dS = \int_V \vec{\nabla} \cdot \vec{\phi}_F dV \quad (\text{A.4})$$

Therefore, Equation (A.2) can be re-written in the form of Equation (A.5):

$$\int_V \frac{\partial \rho F}{\partial t} dV + \int_V \vec{\nabla} \cdot \vec{\phi}_F dV = \int_V q_F dV + \int_V p_F dV \quad (\text{A.5})$$

Finally, considering an infinitesimally small volume element dV instead of the volume V , Equation (A.5) can be converted to the general Equation (A.6) that

represents the conservation of the variable F .

$$\frac{\partial \rho_F(\vec{r}, t)}{\partial t} + \vec{\nabla} \cdot \vec{\phi}_F = q_F + p_F \quad (\text{A.6})$$

A.2 Conservation equations for premixed, laminar and one-dimensional flames

An one-dimensional laminar premixed flame is a flame in which each flame parameter is varying only in one direction z that is perpendicular to the burner surface. This flame is stationary that means no temporal dependence. Finally the effects due to the gravity represented by p_F are negligible (Equation (A.6)) and the radiation, that is quite important in reacting flows but we do not solve the energy equation as we measure, the experimental temperature profile. The simplified general conservation equation for premixed, laminar and one-dimensional flames is presented in Equation (A.7):

$$\frac{\partial \vec{\phi}_F}{\partial z} = q_F \quad (\text{A.7})$$

$\frac{\partial \vec{\phi}_F}{\partial z}$ represents the variation of the density flux of an extensive variable F versus the z -axis. q_F represents sources and sinks that respectively produce and consume F within a flame element.

Equation (A.7) will be applied to the conservation of mass, chemical species and enthalpy in flames of the present work following the Warnatz approach [84]. The following sections describe this approach.

A.2.1 Mass conservation equation

In Equation (A.7), the left side represents the total mass flux density. This total mass flux density is a product of the total mass density ρ and the velocity v of the considered flow. The term of the right side is null due to the conservation of mass. Therefore the product ρv is constant all along the flame. Then Equation (A.8) represents the conservation of the total mass in the flame:

$$\frac{\partial(\rho v)}{\partial z} = 0 \quad (\text{A.8})$$

A.2.2 Mass conservation of chemical species

In the same way as the total mass flux is represented by $\vec{\phi}_m = \rho v$, the mass flux density of a chemical species i is given by $\vec{\phi}_{m_i} = \rho_i v_i$. The mass density of species ρ_i is given by the product of the total mass density and its mass fraction ($\rho_i = \rho w_i$), the mass flux density can be written as: $\vec{\phi}_{m_i} = \rho w_i v_i$.

In contrast with the case where F is the total mass of the mixture, the mass of i species is produced and consumed through chemical reactions. The term q_{m_i} of Equation (A.7) is not null. This term corresponds to r_i that describes the mass rate production of i species through chemical reactions as depicted in Equation (A.9):

$$r_i = M_i \cdot \frac{\partial [i]}{\partial t} \quad (\text{A.9})$$

In Equation (A.9) M_i represents the molecular mass of species i and $[i]$ its molar concentration.

The conservation Equation (A.10) of the mass of a chemical species, taking into account all the previous considerations, is:

$$\frac{\partial(\rho w_i v_i)}{\partial z} = r_i \quad (\text{A.10})$$

The flow velocity v_i of a species i depends of the total flux velocity v representing the convection of i in the reacting flow and a diffusion velocity V_i that described the diffusion effect. This diffusion effect is due to concentration gradients of species inside the flame. Using these two parameters, the flow velocity can be represented by : $v_i = v + V_i$ and once inserted in Equation (A.10) after a simple law of differentiation gives Equation (A.11):

$$w_i \frac{\partial(\rho v)}{\partial z} + \rho v \frac{\partial(w_i)}{\partial z} + \frac{\partial(\rho w_i V_i)}{\partial z} = r_i \quad (\text{A.11})$$

The first term of Equation (A.11) is null from the conservation equation of the total mass, the product between ρ and v is constant at each position in the flame. Then Equation (A.11) gives Equation (A.12) by defining the flux diffusion $j_i = \rho w_i V_i$:

$$\rho v \frac{\partial(w_i)}{\partial z} + \frac{\partial(j_i)}{\partial z} = r_i \quad (\text{A.12})$$

A.2.3 Conservation energy equation

The energy flux density of the reacting mixture is given by $\sum_i \rho w_i v_i h_i + j_q$ where h_i is the specific enthalpy of the species i and j_q represents the heat flux density that is caused by the energy transport in the flame. In the same way, chemical reactions neither create or destroy energy but transform it. Therefore, the term at the right hand side of the conservation energy is null, and then the conservation of energy gives:

$$\sum_i \frac{\partial(\rho w_i v_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p h_i \quad (\text{A.13})$$

In Equation (A.13), the term $p h_i$ represents the energy lost by flame radiation and by heat transfer to the burner surface and the wall of the combustion chamber. Flame radiations are significant in the rich flame where soot are formed and not significant in the lean flame. The heat transfer to the wall of the combustion chamber depends on the position of the flame and it is expected to be significant in all the flames. As mentioned before, $v_i = v + V_i$ and $j_i = \rho w_i V_i$ then Equation (A.13) gives:

$$\sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(j_i h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p h_i \quad (\text{A.14})$$

The first two terms of Equation (A.14) at the left hand side can be developed by the product derivation law, as depicted in Equation (A.15):

$$\begin{aligned} \sum_i \frac{\partial(\rho v w_i h_i)}{\partial z} + \sum_i \frac{\partial(j_i h_i)}{\partial z} = & \\ & \left(\sum_i w_i h_i \frac{\partial(\rho v)}{\partial z} + \rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \rho v \sum_i h_i \frac{\partial(w_i)}{\partial z} \right) \\ & + \left(\sum_i h_i \frac{\partial(j_i)}{\partial z} + \sum_i j_i \frac{\partial(h_i)}{\partial z} \right) \quad (\text{A.15}) \end{aligned}$$

By introducing Equations (A.8) and (A.15) into Equation (A.14), we obtain the Equation (A.16):

$$\rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \rho v \sum_i h_i \frac{\partial(w_i)}{\partial z} + \sum_i h_i \frac{\partial(j_i)}{\partial z} + \sum_i j_i \frac{\partial(h_i)}{\partial z} + \frac{\partial j_q}{\partial z} = p h_i \quad (\text{A.16})$$

Finally, considering the mass conservation Equation (A.12) of species i ,

Equation (A.16) can be simplified into the enthalpy conservation Equation (A.17):

$$\rho v \sum_i w_i \frac{\partial(h_i)}{\partial z} + \sum_i h_i r_i + \sum_i j_i \frac{\partial(h_i)}{\partial z} + \frac{\partial(j_q)}{\partial z} = p h_i \quad (\text{A.17})$$

Where $\sum_i h_i r_i$ represents the change in enthalpy due to the production of species i through chemical reactions. j_i and j_q represent the enthalpy brought by the diffusion of species i and the heat flux caused by temperature gradient, respectively.

To introduce the temperature T in Equation (A.17), we note that $dh_i = c_{p,i} dT$, then Equation (A.17) gives Equation (A.18):

$$\rho v \sum_i w_i c_{p,i} \frac{\partial T}{\partial z} + \sum_i h_i r_i + \sum_i j_i c_{p,i} \frac{\partial T}{\partial z} + \frac{\partial j_q}{\partial z} = p h_i \quad (\text{A.18})$$

A.2.4 Heat and mass transport phenomena

Empiric observations notice that a gradient of concentration generates a mass transport called "*molecular diffusion*", similarly a gradient of temperature leads to a heat transfer called "*heat conduction*". These observations have already been explained in the theory of none reversible thermodynamic by Hirschfelder et al. [128].

The molecular diffusion j_i can be obtained by extending Fick's law in Equation (A.19):

$$j_i = \frac{c^2}{\rho} M_i \sum_j M_j D_{ij} \frac{\partial x_j}{\partial z} - \frac{D_i^T}{T} \frac{\partial T}{\partial z} \quad (\text{A.19})$$

Where c is the molar concentration, M_i and M_j are molecular masses of species i and j , D_{ij} is the binary diffusion coefficient, x_j is the mole fraction of species j and D_i^T is the thermal diffusion coefficient of species i .

For the heat conduction, the term j_q can be obtained by Fourier's law, as depicted in Equation (A.20), where λ represents the heat conductivity of the mixture.

$$j_q = -\lambda \frac{\partial T}{\partial z} \quad (\text{A.20})$$

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The determination of the D_{ij} and D_i^T coefficients and λ is given in the chapter developing the *Cosilab*® software.

Appendix B

Katshiatshia ethyl valerate mechanism

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
H + O ₂ ⇌OH + O	1.040e+14	0.000	15290.00
H ₂ + O⇌H + OH	5.080e+04	2.670	6292.00
OH + H ₂ ⇌H ₂ O + H	4.380e+13	0.000	6990.00
H ₂ O + O⇌OH + OH	2.970e+06	2.020	13400.00
H ₂ + M⇌H + H + M	4.577e+19	-1.400	104400.00
Enhanced Collision. Efficiencies: H ₂ O = 12, H ₂ = 2.5, CO = 1.9, CO ₂ = 3.8			
O + O + M⇌O ₂ + M	6.165e+15	-0.500	0.00
Enhanced Collision. Efficiencies: H ₂ O = 12, H ₂ = 2.5, CO = 1.9, CO ₂ = 3.8			
H + OH + M⇌H ₂ O + M	3.500e+22	-2.000	0.00
Enhanced Collision. Efficiencies: H ₂ O = 3.65, H ₂ = 0.73, CO = 1.9, CO ₂ = 3.8			
H + O ₂ + (M)⇌HO ₂ + (M)	4.650e+12	0.440	0.00
Low pressure limit	1.737e+19	-1.230	0.00
TROE 6.700e-01, 1.000e-30 1.000e+30, 1.000e+30			
Enhanced Collision. Efficiencies: H ₂ O = 10, H ₂ = 1.3, CO = 1.9			
Enhanced Collision. Efficiencies: CO ₂ = 3.8, Ar = 0.00			
H + HO ₂ ⇌OH + OH	7.079e+13	0.000	295.00
H ₂ + O ₂ ⇌H + HO ₂	5.176e+05	2.430	53500.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{HO}_2 + \text{O} \rightleftharpoons \text{O}_2 + \text{OH}$	3.250e+13	0.000	0.00
$\text{OH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}_2$	2.456e+13	0.000	-497.00
$\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$	1.300e+11	0.000	-1630.00
Duplicate Reaction			
$\text{HO}_2 + \text{HO}_2 \rightleftharpoons \text{O}_2 + \text{H}_2\text{O}_2$	3.658e+14	0.000	12000.00
Duplicate Reaction			
$\text{H}_2\text{O}_2(+ \text{M}) \rightleftharpoons \text{OH} + \text{OH}(+ \text{M})$	2.000e+12	0.900	48750.00
Low pressure limit	2.490e+24	-2.300	48750.00
<i>Enhanced Collision. Efficiencies: $\text{H}_2 = 3.7$, $\text{O}_2 = 1.2$, $\text{CO} = 2.8$, $\text{CO}_2 = 1.6$</i>			
$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{HO}_2 + \text{H}_2$	2.150e+10	1.000	6000.00
$\text{OH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2 + \text{H}_2\text{O}$	1.740e+12	0.000	318.00
Duplicate Reaction			
$\text{OH} + \text{H}_2\text{O}_2 \rightleftharpoons \text{HO}_2 + \text{H}_2\text{O}$	7.590e+13	0.000	7269.00
Duplicate Reaction			
$\text{H} + \text{O} + \text{M} \rightleftharpoons \text{OH} + \text{M}$	4.714e+18	-1.000	0.00
<i>Enhanced Collision. Efficiencies: $\text{H}_2\text{O} = 12$, $\text{H}_2 = 2.5$, $\text{CO} = 1.5$, $\text{CO}_2 = 2$</i>			
$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	7.015e+04	2.050	-355.70
Duplicate Reaction			
$\text{CO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}$	5.757e+12	-0.660	331.80
Duplicate Reaction			
$\text{H} + \text{CH}_2\text{O} \rightleftharpoons \text{HCO} + \text{H}_2$	1.260e+08	1.620	2170.00
$\text{O} + \text{CH}_2\text{O} \rightleftharpoons \text{HCO} + \text{OH}$	1.070e+13	0.570	2762.00
$\text{OH} + \text{CH}_2\text{O} \rightleftharpoons \text{HCO} + \text{H}_2\text{O}$	1.800e+13	0.000	436.00
$\text{CH}_2\text{O} + \text{M} \rightleftharpoons \text{HCO} + \text{H} + \text{M}$	3.300e+39	-6.300	99904.00
<i>Enhanced Collision. Efficiencies: $\text{Ar} = 0.7$, $\text{H}_2 = 2$, $\text{CO} = 1.5$, $\text{CH}_2\text{O} = 3$</i>			
$\text{H} + \text{HCO} \rightleftharpoons \text{CO} + \text{H}_2$	7.340e+13	0.000	0.00
$\text{O} + \text{HCO} \rightleftharpoons \text{CO}_2 + \text{H}$	3.000e+13	0.000	0.00
$\text{O} + \text{HCO} \rightleftharpoons \text{CO} + \text{OH}$	3.020e+13	0.000	0.00
$\text{OH} + \text{HCO} \rightleftharpoons \text{CO} + \text{H}_2\text{O}$	1.020e+14	0.000	0.00
$\text{O}_2 + \text{HCO} \rightleftharpoons \text{CO} + \text{HO}_2$	7.580e+12	0.000	410.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
HCO + M $\rightleftharpoons$ CO + H + M	4.750e+11	0.660	14870.00
<i>Enhanced Collision. Efficiencies: H₂O = 12, H₂ = 2, CO = 1.5, CO₂ = 2</i>			
H + CH ₂ $\rightleftharpoons$ CH + H ₂	6.020e+12	0.000	-1789.00
O + CH ₂ $\rightleftharpoons$ CO + H + H	1.200e+14	0.000	0.00
O ₂ + CH ₂ $\rightleftharpoons$ CO ₂ + H + H	2.470e+13	0.000	1491.00
O + CH $\rightleftharpoons$ CO + H	3.970e+13	0.000	0.00
O ₂ + CH $\rightleftharpoons$ CO + OH	3.310e+13	0.000	0.00
H + HCCO $\rightleftharpoons$ CH ₂ (s) + CO	1.000e+14	0.000	0.00
O + HCCO $\rightleftharpoons$ CO + CO + H	9.640e+13	0.000	0.00
HCCO + OH $\Rightarrow$ HCO + CO + H	1.000e+14	0.000	0.00
HCCO + O ₂ $\Rightarrow$ CO + CO + OH	1.630e+12	0.000	855.00
CH + CO ₂ $\rightleftharpoons$ HCO + CO	3.400e+12	0.000	690.00
CO + O(+ M) $\rightleftharpoons$ CO ₂ (+ M)	1.362e+10	0.000	2384.00
Low pressure limit	1.173e+24	-2.790	4191.00
<i>Enhanced Collision. Efficiencies: H₂O = 12, H₂ = 2, CO = 1.75, CO₂ = 3.6</i>			
CO + O ₂ $\rightleftharpoons$ CO ₂ + O	1.119e+12	0.000	47700.00
HO ₂ + CO $\rightleftharpoons$ CO ₂ + OH	1.570e+05	2.180	17940.00
CH ₂ + CH ₂ $\rightleftharpoons$ C ₂ H ₂ + H ₂	1.200e+14	0.000	795.00
CH ₃ + CH ₂ $\rightleftharpoons$ C ₂ H ₄ + H	4.220e+13	0.000	0.00
CH ₂ (s) + M $\rightleftharpoons$ CH ₂ + M	1.000e+13	0.000	0.00
<i>Enhanced Collision. Efficiencies: H = 0, H₂O = 0, C₂H₂ = 0</i>			
CH ₂ (s) + CH ₄ $\rightleftharpoons$ 2CH ₃	4.000e+13	0.000	0.00
CH ₂ (s) + C ₂ H ₆ $\rightleftharpoons$ CH ₃ + C ₂ H ₅	1.200e+14	0.000	0.00
CH ₂ (s) + O ₂ $\rightleftharpoons$ CO + OH + H	7.000e+13	0.000	0.00
CH ₂ (s) + H ₂ O $\rightleftharpoons$ CH ₃ + OH	7.500e+06	2.000	5000.00
CH ₂ (s) + H ₂ O $\rightleftharpoons$ CH ₂ + H ₂ O	3.000e+13	0.000	0.00
CH ₂ (s) + C ₂ H ₂ $\rightleftharpoons$ CH ₂ + C ₂ H ₂	4.000e+13	0.000	0.00
CH ₂ (s) + H $\rightleftharpoons$ CH ₂ + H	2.000e+14	0.000	0.00
CH ₂ (s) + O $\rightleftharpoons$ CO + 2 H	3.000e+13	0.000	0.00
CH ₂ (s) + OH $\rightleftharpoons$ CH ₂ O + H	3.000e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2(\text{s}) + \text{H} \rightleftharpoons \text{CH} + \text{H}_2$	3.000e+13	0.000	0.00
$\text{CH}_2(\text{s}) + \text{CO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CO}$	1.400e+13	0.000	0.00
$\text{CH}_2(\text{s}) + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$	2.000e+13	0.000	0.00
$\text{CH}_2(\text{s}) + \text{CH}_2\text{CO} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CO}$	1.600e+14	0.000	0.00
$\text{O} + \text{CH}_2\text{CO} \rightleftharpoons \text{HCO} + \text{HCO}$	2.290e+12	0.000	1352.00
$\text{CH}_2\text{CO} + \text{M} \rightleftharpoons \text{CH}_2 + \text{CO} + \text{M}$	1.000e+16	0.000	59324.00
$\text{CH}_3\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CO} + \text{HO}_2$	3.000e+13	0.000	39100.00
$\text{CH}_3\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_3\text{CO} + \text{H}_2\text{O}$	2.350e+10	0.730	-1110.00
$\text{CH}_3\text{CHO} + \text{O} \rightleftharpoons \text{CH}_3\text{CO} + \text{OH}$	5.800e+12	0.000	1800.00
$\text{CH}_3\text{CHO} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_4$	2.000e-06	5.600	2460.00
$\text{CH}_3\text{CO} + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{OH}$	3.900e+13	0.000	0.00
$\text{CH}_3\text{CO} + \text{O} \rightleftharpoons \text{CH}_3 + \text{CO}_2$	1.000e+13	0.000	0.00
$\text{CH}_3\text{CO} + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2\text{O}$	1.200e+13	0.000	0.00
$\text{CH}_3\text{CO} + \text{OH} \rightleftharpoons \text{CH}_3 + \text{CO} + \text{OH}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CO} + \text{HO}_2 \rightleftharpoons \text{CH}_3 + \text{CO}_2 + \text{OH}$	3.000e+13	0.000	0.00
$\text{CH}_3 + \text{HCO} \rightleftharpoons \text{CH}_3\text{CHO}$	1.800e+13	0.000	0.00
$\text{H} + \text{CH}_4 \rightleftharpoons \text{H}_2 + \text{CH}_3$	1.320e+04	3.000	8041.00
$\text{O} + \text{CH}_4 \rightleftharpoons \text{OH} + \text{CH}_3$	9.030e+08	1.560	8489.00
$\text{OH} + \text{CH}_4 \rightleftharpoons \text{H}_2\text{O} + \text{CH}_3$	1.560e+07	1.830	2783.00
$\text{CH}_3 + \text{H} + \text{M} \rightleftharpoons \text{CH}_4 + \text{M}$	8.000e+26	-3.000	0.00
<i>Enhanced Collision. Efficiencies: $\text{H}_2 = 2$, $\text{CO} = 2$, $\text{CO}_2 = 3$, $\text{H}_2\text{O} = 5$</i>			
$\text{CH}_2 + \text{H}_2 \rightleftharpoons \text{CH}_3 + \text{H}$	7.000e+13	0.000	0.00
$\text{O} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{O} + \text{H}$	8.430e+13	0.000	0.00
$\text{O}_2 + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{O} + \text{OH}$	3.310e+11	0.000	8946.00
$\text{OH} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2$	8.000e+12	0.000	0.00
$\text{OH} + \text{CH}_3 \rightleftharpoons \text{CH}_2 + \text{H}_2\text{O}$	3.610e+13	0.000	0.00
$\text{CH}_3 + \text{CH}_2\text{O} \rightleftharpoons \text{HCO} + \text{CH}_4$	4.090e+12	0.000	8847.00
$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_6$	9.973e+25	-3.890	5100.00
$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{H}$	8.920e+11	-0.005	11850.00
$\text{CH}_3 + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2$	1.000e+16	0.000	32013.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_2H_3 + O_2 \rightleftharpoons C_2H_2 + HO_2$	1.000e+11	0.000	0.00
$C_2H_3 + OH \rightleftharpoons C_2H_2 + H_2O$	2.000e+13	0.000	0.00
$O + C_2H_3 \rightleftharpoons CH_2CO + H$	3.000e+13	0.000	0.00
$C_2H_3 + H \rightleftharpoons C_2H_2 + H_2$	1.200e+13	0.000	0.00
$H + C_2H_2 (+ M) \rightleftharpoons C_2H_3 (+ M)$	5.600e+12	0.000	2400.00
Low pressure limit	3.800e+40	-7.270	7220.00
Troe parameters: a=0.7507, T***=98.5, T*=1302, T**=4167			
$H_2 + C_2H \rightleftharpoons H + C_2H_2$	4.900e+05	2.500	560.00
$O + C_2H_2 \rightleftharpoons CH_2 + CO$	6.940e+06	2.000	1900.00
$O + C_2H_2 \rightleftharpoons HCCO + H$	1.350e+07	2.000	1900.00
$OH + C_2H_2 \rightleftharpoons CH_2CO + H$	2.180e-04	4.500	-1000.00
$OH + C_2H_2 \rightleftharpoons H_2O + C_2H$	3.370e+07	2.000	14000.00
$C_2H + O \rightleftharpoons CO + CH$	1.020e+13	0.000	0.00
$C_2H + O_2 \rightleftharpoons CO + CO + H$	3.520e+13	0.000	0.00
$C_2H + O_2 \rightleftharpoons CO + HCO$	5.000e+13	0.000	1500.00
$C_2H + CO_2 \rightleftharpoons HCCO + CO$	2.000e+12	0.000	0.00
$O_2 + C_2H_3 \rightleftharpoons CH_2O + HCO$	5.420e+12	0.000	0.00
$C_2H_2 + O \rightleftharpoons C_2H + OH$	3.160e+15	-0.600	15000.00
$CH + CH_2 \rightleftharpoons C_2H_2 + H$	4.000e+13	0.000	0.00
$C_2H_3 + CH_2 \rightleftharpoons C_2H_2 + CH_3$	3.000e+13	0.000	0.00
$C_2H_3 + C_2H \rightleftharpoons C_2H_2 + C_2H_2$	3.000e+13	0.000	0.00
$C_2H_3 + CH \rightleftharpoons CH_2 + C_2H_2$	5.000e+13	0.000	0.00
$OH + C_2H_2 \rightleftharpoons HCCOH + H$	5.040e+05	2.300	13500.00
$HCCOH + H \rightleftharpoons H + CH_2CO$	1.000e+13	0.000	0.00
$OH + C_2H_2 \rightleftharpoons CH_3 + CO$	4.830e-04	4.000	-2000.00
$CH + HCCO \rightleftharpoons C_2H_2 + CO$	5.000e+13	0.000	0.00
$HCCO + HCCO \rightleftharpoons C_2H_2 + CO + CO$	1.000e+13	0.000	0.00
$C_2H_2 + O_2 \rightleftharpoons HCCO + OH$	2.000e+08	1.500	30100.00
$CH + C_2H_2 \rightleftharpoons C_3H_2 + H$	1.000e+14	0.000	0.00
$HCCO + C_2H_2 \rightleftharpoons C_3H_3 + CO$	1.000e+11	0.000	3000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2(\text{s}) + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}$	1.500e+14	0.000	0.00
$\text{CH}_3 + \text{C}_2\text{H} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}$	2.410e+13	0.000	0.00
$\text{CH}_2 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}$	1.000e+12	0.000	0.00
$\text{C}_3\text{H}_3 + \text{H} \rightleftharpoons \text{CH}_2 + \text{C}_2\text{H}_2$	1.010e+13	0.000	15795.00
$\text{C}_2\text{H}_4 + \text{O} \rightleftharpoons \text{HCO} + \text{CH}_3$	4.720e+06	1.880	182.00
$\text{OH} + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	2.050e+13	0.000	5944.00
$\text{H} + \text{C}_2\text{H}_4 \rightleftharpoons \text{H}_2 + \text{C}_2\text{H}_3$	2.000e+15	0.000	2007.00
$\text{C}_2\text{H}_4 + \text{M} \rightleftharpoons \text{C}_2\text{H}_2 + \text{H}_2 + \text{M}$	1.500e+15	0.000	55800.00
<i>Enhanced Collision. Efficiencies: H₂ = 2, H₂O = 5, CO = 2, CO₂ = 3</i>			
$\text{CH}_3 + \text{C}_2\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_4$	6.140e+06	1.740	10450.00
$\text{H} + \text{C}_2\text{H}_6 \rightleftharpoons \text{H}_2 + \text{C}_2\text{H}_5$	1.150e+08	1.900	7530.00
$\text{O} + \text{C}_2\text{H}_6 \rightleftharpoons \text{OH} + \text{C}_2\text{H}_5$	1.000e+09	1.500	5805.00
$\text{OH} + \text{C}_2\text{H}_6 \rightleftharpoons \text{H}_2\text{O} + \text{C}_2\text{H}_5$	7.230e+06	2.000	865.00
$\text{O} + \text{C}_2\text{H}_5 \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}$	6.620e+13	0.000	0.00
$\text{O}_2 + \text{C}_2\text{H}_5 \rightleftharpoons \text{HO}_2 + \text{C}_2\text{H}_4$	1.020e+11	0.000	-2186.00
$\text{C}_3\text{H}_2 + \text{O} \rightleftharpoons \text{C}_2\text{H}_2 + \text{CO}$	6.800e+13	0.000	0.00
$\text{C}_3\text{H}_2 + \text{OH} \rightleftharpoons \text{HCO} + \text{C}_2\text{H}_2$	1.000e+13	0.000	0.00
$\text{C}_3\text{H}_2 + \text{O}_2 \rightleftharpoons \text{HCCO} + \text{H} + \text{CO}$	5.000e+13	0.000	0.00
$\text{C}_3\text{H}_2 + \text{CH} \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}$	5.000e+13	0.000	0.00
$\text{C}_3\text{H}_2 + \text{CH}_2 \rightleftharpoons \text{NC}_4\text{H}_3 + \text{H}$	5.000e+13	0.000	0.00
$\text{C}_3\text{H}_2 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}$	5.000e+12	0.000	0.00
$\text{C}_3\text{H}_2 + \text{HCCO} \rightleftharpoons \text{NC}_4\text{H}_3 + \text{CO}$	1.000e+13	0.000	0.00
$\text{C}_3\text{H}_3 + \text{H} \rightleftharpoons \text{C}_3\text{H}_2 + \text{H}_2$	1.200e+14	0.000	1000.00
$\text{C}_3\text{H}_3 + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{C}_2\text{H}$	2.000e+13	0.000	0.00
$\text{C}_3\text{H}_3 + \text{OH} \rightleftharpoons \text{C}_3\text{H}_2 + \text{H}_2\text{O}$	5.000e+12	0.000	0.00
$\text{C}_3\text{H}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{HCO}$	3.000e+10	0.000	2868.00
$\text{C}_3\text{H}_3 + \text{HO}_2 \rightleftharpoons \text{OH} + \text{CO} + \text{C}_2\text{H}_3$	8.000e+11	0.000	0.00
$\text{C}_3\text{H}_3 + \text{HCCO} \rightleftharpoons \text{C}_4\text{H}_4 + \text{CO}$	2.500e+13	0.000	0.00
$\text{C}_3\text{H}_3 + \text{CH} \rightleftharpoons \text{iC}_4\text{H}_3 + \text{H}$	5.000e+13	0.000	0.00
$\text{C}_3\text{H}_3 + \text{CH}_2 \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}$	5.000e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_2\text{H}_3 + \text{CH}_2 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{H}$	3.000e+13	0.000	0.00
$\text{C}_2\text{H}_3 + \text{CH}_2 \rightleftharpoons \text{C}_3\text{H}_4 - \text{P} + \text{H}$	3.000e+13	0.000	0.00
$\text{C}_2\text{H}_2 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{H}$	5.140e+09	0.860	22153.00
$\text{C}_3\text{H}_6 + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CH}_3$	4.520e+12	0.000	0.00
$\text{C}_3\text{H}_6 + \text{H} \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{H}_2$	6.460e+12	0.000	4445.00
$\text{C}_3\text{H}_6 + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$	1.200e+08	1.650	327.00
$\text{C}_3\text{H}_6 + \text{O} \rightleftharpoons \text{C}_2\text{H}_5 + \text{HCO}$	3.500e+07	1.650	-972.00
$\text{C}_3\text{H}_6 + \text{O} \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{OH}$	1.800e+11	0.700	5880.00
$\text{C}_3\text{H}_6 + \text{OH} \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{H}_2\text{O}$	3.100e+06	2.000	-298.00
$\text{C}_3\text{H}_6 + \text{HO}_2 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{H}_2\text{O}_2$	9.600e+03	2.600	13910.00
$\text{C}_3\text{H}_6 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{CH}_4$	2.200e+00	3.500	5675.00
$\text{C}_3\text{H}_6 \rightleftharpoons \text{C}_2\text{H}_3 + \text{CH}_3$	1.100e+21	-1.200	97720.00
$\text{C}_3\text{H}_5 - \text{A} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_2\text{O}$	1.060e+10	0.340	12838.00
$\text{CH}_3 + \text{C}_2\text{H}_2 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A}$	2.680e+53	-12.820	35730.00
$\text{C}_2\text{H}_3 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{H}$	2.570e+13	0.000	0.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{CH}_3$	3.900e+32	-5.220	19747.00
$\text{C}_3\text{H}_8 + \text{H} \rightleftharpoons \text{H}_2 + \text{NC}_3\text{H}_7$	1.300e+06	2.540	6756.00
$\text{C}_3\text{H}_8 + \text{H} \rightleftharpoons \text{H}_2 + \text{iC}_3\text{H}_7$	1.300e+06	2.400	4471.00
$\text{C}_3\text{H}_8 + \text{O} \rightleftharpoons \text{NC}_3\text{H}_7 + \text{OH}$	1.900e+05	2.680	3716.00
$\text{C}_3\text{H}_8 + \text{O} \rightleftharpoons \text{iC}_3\text{H}_7 + \text{OH}$	4.760e+04	2.710	2106.00
$\text{C}_3\text{H}_8 + \text{OH} \rightleftharpoons \text{NC}_3\text{H}_7 + \text{H}_2\text{O}$	1.400e+03	2.660	527.00
$\text{C}_3\text{H}_8 + \text{OH} \rightleftharpoons \text{iC}_3\text{H}_7 + \text{H}_2\text{O}$	2.700e+04	2.390	393.00
$\text{C}_3\text{H}_8 + \text{HO}_2 \rightleftharpoons \text{NC}_3\text{H}_7 + \text{H}_2\text{O}_2$	4.760e+04	2.550	16490.00
$\text{C}_3\text{H}_8 + \text{HO}_2 \rightleftharpoons \text{iC}_3\text{H}_7 + \text{H}_2\text{O}_2$	9.640e+03	2.600	13910.00
$\text{C}_3\text{H}_8 + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{NC}_3\text{H}_7$	9.030e-01	3.650	7153.00
$\text{C}_3\text{H}_8 + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{iC}_3\text{H}_7$	1.510e+00	3.460	5480.00
$\text{NC}_3\text{H}_7 + \text{H} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_3$	3.700e+24	-2.920	12505.00
$\text{NC}_3\text{H}_7 + \text{H} \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$	1.800e+12	0.000	0.00
$\text{NC}_3\text{H}_7 + \text{O}_2 \rightleftharpoons \text{C}_3\text{H}_6 + \text{HO}_2$	9.000e+10	0.000	0.00
$\text{NC}_3\text{H}_7 + \text{HO}_2 \rightleftharpoons \text{C}_2\text{H}_5 + \text{OH} + \text{CH}_2\text{O}$	2.400e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{NC}_3\text{H}_7 + \text{HCO} \rightleftharpoons \text{C}_3\text{H}_8 + \text{CO}$	6.000e+13	0.000	0.00
$\text{NC}_3\text{H}_7 + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{C}_3\text{H}_6$	1.100e+13	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{H} \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_5$	1.400e+28	-3.940	15916.00
$\text{iC}_3\text{H}_7 + \text{H} \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2$	3.200e+12	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{O} \rightleftharpoons \text{CH}_3\text{CHO} + \text{CH}_3$	9.600e+13	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{OH} \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	2.400e+13	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{O}_2 \rightleftharpoons \text{C}_3\text{H}_6 + \text{HO}_2$	1.300e+11	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{CH}_3 + \text{OH}$	2.400e+13	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{HCO} \rightleftharpoons \text{C}_3\text{H}_8 + \text{CO}$	1.200e+14	0.000	0.00
$\text{iC}_3\text{H}_7 + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{C}_3\text{H}_6$	2.200e+14	-0.680	0.00
$\text{CH}_3 + \text{C}_2\text{H}_4 \rightleftharpoons \text{NC}_3\text{H}_7$	3.300e+11	0.000	7700.00
$\text{C}_4\text{H}_2 + \text{H} \rightleftharpoons \text{C}_2\text{H}_2 + \text{C}_2\text{H}$	5.000e+13	0.000	0.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H} \rightleftharpoons \text{NC}_4\text{H}_3$	1.300e+30	-6.120	2510.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H} \rightleftharpoons \text{iC}_4\text{H}_3$	2.600e+44	-9.470	14650.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}$	1.580e+13	0.000	25000.00
$\text{C}_2\text{H}_4 + \text{C}_2\text{H} \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}$	1.200e+13	0.000	0.00
$\text{C}_4\text{H}_4 + \text{C}_2\text{H} \rightleftharpoons \text{C}_4\text{H}_2 + \text{C}_2\text{H}_3$	1.000e+13	0.000	0.00
$\text{C}_4\text{H}_2 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_4\text{H}_4 + \text{C}_2\text{H}$	1.570e+13	0.000	27502.00
$\text{NC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{iC}_4\text{H}_3 + \text{H}$	2.500e+20	-1.670	10800.00
$\text{NC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	6.300e+25	-3.340	10014.00
$\text{iC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	2.800e+23	-2.550	10780.00
$\text{NC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_4\text{H}_4$	2.000e+47	-10.260	13070.00
$\text{iC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_4\text{H}_4$	3.400e+43	-9.010	12120.00
$\text{C}_4\text{H} + \text{H}_2 \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}$	4.900e+05	2.500	560.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 \rightleftharpoons \text{NC}_4\text{H}_5$	1.100e+32	-7.330	6200.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_3 \rightleftharpoons \text{iC}_4\text{H}_5$	1.600e+46	-10.980	18600.00
$\text{C}_4\text{H}_6 + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_2\text{H}_3$	2.000e+12	0.000	0.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_4\text{H}_6$	1.500e+42	-8.840	12483.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightleftharpoons \text{iC}_4\text{H}_5 + \text{H}$	1.200e+22	-2.440	13654.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_3 \rightleftharpoons \text{NC}_4\text{H}_5 + \text{H}$	2.400e+20	-2.040	15361.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{NC}_4\text{H}_5 \rightleftharpoons \text{iC}_4\text{H}_5$	1.500e+67	-16.890	59100.00
$\text{NC}_4\text{H}_5 + \text{H} \rightleftharpoons \text{iC}_4\text{H}_5 + \text{H}$	3.100e+26	-3.350	17423.00
$\text{C}_4\text{H}_6 \rightleftharpoons \text{iC}_4\text{H}_5 + \text{H}$	5.700e+36	-6.270	112350.00
$\text{iC}_4\text{H}_5 + \text{H} \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}_2$	3.000e+13	0.000	0.00
$\text{iC}_4\text{H}_5 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}_2\text{O}$	4.000e+12	0.000	0.00
$\text{NC}_4\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{CO} + \text{HCO}$	4.160e+10	0.000	2500.00
$\text{iC}_4\text{H}_5 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_2\text{CHO}$	7.860e+16	-1.800	0.00
$\text{NC}_4\text{H}_5 + \text{HCO} \rightleftharpoons \text{C}_4\text{H}_6 + \text{CO}$	9.000e+13	0.000	0.00
$\text{iC}_4\text{H}_5 + \text{HCO} \rightleftharpoons \text{C}_4\text{H}_6 + \text{CO}$	9.000e+13	0.000	0.00
$\text{C}_4\text{H}_6 + \text{O} \rightleftharpoons \text{HCO} + \text{C}_3\text{H}_5 - \text{A}$	6.000e+08	1.450	-860.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H}_5 \Rightarrow \text{C}_4\text{H}_6 + \text{H}$	1.100e+12	0.000	16636.00
$\text{C}_4\text{H}_6 + \text{H} \Rightarrow \text{C}_2\text{H}_2 + \text{C}_2\text{H}_5$	5.790e+12	0.000	3103.00
$\text{C}_3\text{H}_3 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_6$	1.500e+12	0.000	0.00
$\text{C}_4\text{H}_8 - 1 + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5$	1.600e+22	-2.390	11180.00
$\text{C}_4\text{H}_8 - 1 + \text{H} \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{H}_2$	6.500e+05	2.540	6756.00
$\text{C}_4\text{H}_8 - 1 + \text{O} \rightleftharpoons \text{NC}_3\text{H}_7 + \text{HCO}$	3.300e+08	1.450	-402.00
$\text{C}_4\text{H}_8 - 1 + \text{O} \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{OH}$	2.600e+13	0.000	4470.00
$\text{C}_4\text{H}_8 - 1 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{H}_2\text{O}$	7.000e+02	2.660	527.00
$\text{C}_4\text{H}_8 - 1 + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{H}_2\text{O}_2$	1.500e+11	0.000	14900.00
$\text{C}_4\text{H}_8 - 1 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{CH}_4$	4.500e-01	3.650	7153.00
$\text{C}_4\text{H}_7 - 1 \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}$	2.280e+52	-12.010	51230.00
$\text{C}_4\text{H}_7 - 1 + \text{H} \rightleftharpoons \text{CH}_3 + \text{C}_3\text{H}_5 - \text{A}$	2.000e+21	-2.000	11000.00
$\text{C}_4\text{H}_7 - 1 + \text{H} \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}_2$	1.800e+12	0.000	0.00
$\text{C}_4\text{H}_7 - 1 + \text{O}_2 \rightleftharpoons \text{C}_4\text{H}_6 + \text{HO}_2$	1.000e+11	0.000	0.00
$\text{C}_4\text{H}_7 - 1 + \text{HCO} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{CO}$	6.000e+13	0.000	0.00
$\text{C}_4\text{H}_7 - 1 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_6 + \text{CH}_4$	1.100e+13	0.000	0.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_4 \rightleftharpoons \text{C}_4\text{H}_7 - 1$	7.930e+38	-8.470	14220.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_4\text{H}_8 - 1$	3.910e+13	0.000	0.00
$\text{C}_3\text{H}_3 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_5\text{H}_5 + \text{H}$	9.630e+40	-7.800	28820.00
$\text{C}_5\text{H}_6 + \text{O}_2 \rightleftharpoons \text{C}_5\text{H}_5 + \text{HO}_2$	5.000e+13	0.000	35400.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_5H_6 + HO_2 \rightleftharpoons C_5H_5 + H_2O_2$	1.990e+12	0.000	11660.00
$C_5H_6 + OH \rightleftharpoons C_5H_5 + H_2O$	3.430e+09	1.200	-447.00
$C_5H_6 + O \rightleftharpoons C_5H_5 + OH$	1.810e+14	0.000	3080.00
$C_5H_6 + H \rightleftharpoons C_5H_5 + H_2$	2.800e+13	0.000	2259.00
$C_5H_6 + CH_3 \rightleftharpoons C_5H_5 + CH_4$	4.160e+12	0.000	11130.00
$C_2H_3 + C_3H_4 - P \rightleftharpoons C_5H_6 + H$	1.000e+13	0.000	1000.00
$C_5H_6 + H \rightleftharpoons C_3H_5 - A + C_2H_2$	1.000e+13	0.000	12000.00
$CH_3OCH_2O \rightleftharpoons CH_2O + CH_3O$	6.480e+12	0.130	14870.00
$CH_3OCH_2O + M \rightleftharpoons CH_3OCHO + H + M$	7.000e+15	0.000	22773.00
$CH_3OCH_2 + M \rightleftharpoons CH_2O + CH_3 + M$	2.620e+16	0.000	82210.00
$CH_3OCHO + M \rightleftharpoons CH_3O + HCO + M$	4.380e+16	0.000	98919.00
$CH_3OCHO + O_2 \rightleftharpoons CH_3OCO + HO_2$	2.000e+14	0.500	42200.00
$CH_3OCHO + OH \rightleftharpoons CH_3OCO + H_2O$	2.340e+07	1.610	-35.00
$CH_3OCHO + H \rightleftharpoons CH_3OCO + H_2$	6.500e+05	2.400	4471.00
$CH_3OCO + M \rightleftharpoons CH_3O + CO + M$	8.640e+15	0.000	14400.00
$CH_3 + CO_2 + M \rightleftharpoons CH_3OCO + M$	1.500e+11	0.000	36730.00
$CH_3 + O_2 \rightleftharpoons CH_3O + O$	2.050e+18	-1.570	29229.00
$CH_3O + H \rightleftharpoons CH_3 + OH$	1.000e+13	0.000	0.00
$CH_3O + M \rightleftharpoons CH_2O + H + M$	1.000e+14	0.000	25000.00
$CH_3O + H \rightleftharpoons CH_2O + H_2$	2.000e+13	0.000	0.00
$CH_3O + OH \rightleftharpoons CH_2O + H_2O$	5.000e+12	0.000	0.00
$CH_3O + O \rightleftharpoons CH_2O + OH$	1.000e+13	0.000	0.00
$CH_3O + O_2 \rightleftharpoons CH_2O + HO_2$	6.300e+10	0.000	2600.00
$CH_3 + CH_3OH \rightleftharpoons CH_3O + CH_4$	1.000e+07	1.500	9940.00
$CH_3O + H \rightleftharpoons CH_2OH + H$	3.400e+06	1.600	0.00
$CH_3OH + OH \rightleftharpoons CH_3O + H_2O$	5.300e+03	2.650	-884.00
$CH_3OH + O \rightleftharpoons CH_3O + OH$	1.300e+05	2.500	5000.00
$CH_3OH + H \rightleftharpoons CH_3O + H_2$	4.000e+12	0.000	6101.00
$CH_3 + CH_3OH \rightleftharpoons CH_2OH + CH_4$	3.000e+07	1.500	9940.00
$O + CH_3OH \rightleftharpoons OH + CH_2OH$	3.880e+05	2.500	3100.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{H} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{H}_2$	1.440e+13	0.000	6095.00
$\text{OH} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{H}_2\text{O}$	4.800e+13	0.000	4500.00
$\text{CH}_2\text{OH} + \text{H} \rightleftharpoons \text{CH}_3 + \text{OH}$	1.000e+13	0.000	0.00
$\text{CH}_2\text{OH} + \text{M} \rightleftharpoons \text{CH}_2\text{O} + \text{H} + \text{M}$	1.000e+14	0.000	25000.00
$\text{CH}_2\text{OH} + \text{H} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2$	2.000e+13	0.000	0.00
$\text{CH}_2\text{OH} + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{H}_2\text{O}$	1.000e+13	0.000	0.00
$\text{CH}_2\text{OH} + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{OH}$	1.000e+13	0.000	0.00
$\text{CH}_2\text{OH} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{HO}_2$	1.000e+14	0.000	5000.00
$\text{CH}_3 + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_4$	1.200e+13	0.000	0.00
$\text{CH}_3\text{O} + \text{CH}_3\text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{CH}_3\text{OH}$	3.010e+11	0.000	4073.00
$\text{CH}_3\text{OH} + \text{H} \rightleftharpoons \text{CH}_3 + \text{H}_2\text{O}$	5.010e+12	0.000	5299.00
$\text{CH}_3\text{OH} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{OH} + \text{H}_2\text{O}_2$	6.310e+12	0.000	19360.00
$\text{CH}_3 + \text{CH}_2\text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_4$	2.410e+12	0.000	0.00
$\text{CH}_3\text{O} + \text{HCO} \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{O}$	6.030e+12	0.000	0.00
$\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_4 + \text{O}_2$	3.600e+12	0.000	0.00
$\text{CH}_4 + \text{O}_2 \rightleftharpoons \text{CH}_3 + \text{HO}_2$	5.177e+15	-0.330	57960.00
$\text{CH}_3 + \text{OH} (+ \text{M}) \rightleftharpoons \text{CH}_3\text{OH} (+ \text{M})$	6.300e+13	0.000	0.00
Low pressure limit	2.700e+38	-6.300	3100.00
Troie parameters: a=0.2105, T***=83.5, T*=5398, T**=8370			
<i>Enhanced Collision. Efficiencies:</i> H ₂ = 2, H ₂ O = 6, CH ₄ = 2			
CO = 1.5, CO ₂ = 2, C ₂ H ₆ = 3			
$\text{CH}_3\text{OCH}_2 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{OH}$	3.730e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{H} \rightleftharpoons \text{C}_2\text{H}_3 + \text{CH}_3$	1.990e+14	0.000	0.00
$\text{CH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$	2.000e+13	0.000	0.00
$\text{CH}_3\text{OCH}_2 + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_3\text{O} + \text{OH}$	1.000e+13	0.000	0.00
$\text{C}_2\text{H}_5\text{OH} (+ \text{M}) \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH} (+ \text{M})$	5.940e+23	-1.680	91163.00
Low pressure limit	2.880e+85	-18.900	109914.00
Troie parameters: a=0.5, T***=200, T*=890, T**=4600			
<i>Enhanced Collision. Efficiencies:</i> H ₂ O = 5, H ₂ = 2, CO ₂ = 3, CO = 2			
$\text{C}_2\text{H}_5\text{OH} (+ \text{M}) \rightleftharpoons \text{C}_2\text{H}_5 + \text{OH} (+ \text{M})$	2.950e+22	-2.200	96600.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
Low pressure limit	3.800e+88	-19.700	115000.00
Troe parameters: a=2.094, T***=16539, T*=1.114, T**=161.36			
$\text{C}_2\text{H}_5\text{OH} + \text{M} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O} + \text{M}$	4.900e+09	1.400	65800.00
Low pressure limit	2.400e+80	-17.900	84800.00
Troe parameters: a=2.126, T***=13568, T*=0.969, T**=160.4			
$\text{C}_2\text{H}_5\text{OH} + \text{M} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2 + \text{M}$	7.240e+11	0.095	91007.00
Low pressure limit	4.460e+87	-19.420	115586.00
Troe parameters: a=0.9, T***=900, T*=1100, T**=3500			
<i>Enhanced Collision. Efficiencies: H₂O = 5</i>			
$\text{C}_2\text{H}_5\text{OH} + \text{OH} \rightleftharpoons \text{PC}_2\text{H}_4\text{OH} + \text{H}_2\text{O}$	6.020e+03	2.680	-576.00
$\text{C}_2\text{H}_5\text{OH} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHOH} + \text{H}_2\text{O}$	1.310e+05	2.430	-1457.00
$\text{C}_2\text{H}_5\text{OH} + \text{OH} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{H}_2\text{O}$	2.810e+02	2.970	-580.00
$\text{C}_2\text{H}_5\text{OH} + \text{H} \rightleftharpoons \text{PC}_2\text{H}_4\text{OH} + \text{H}_2$	1.880e+03	3.200	7150.00
$\text{C}_2\text{H}_5\text{OH} + \text{H} \rightleftharpoons \text{CH}_3\text{CHOH} + \text{H}_2$	1.790e+05	2.530	3420.00
$\text{C}_2\text{H}_5\text{OH} + \text{H} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{H}_2$	5.550e-23	10.600	-4459.00
$\text{C}_2\text{H}_5\text{OH} + \text{O} \rightleftharpoons \text{PC}_2\text{H}_4\text{OH} + \text{OH}$	9.410e+07	1.700	5459.00
$\text{C}_2\text{H}_5\text{OH} + \text{O} \rightleftharpoons \text{CH}_3\text{CHOH} + \text{OH}$	1.880e+07	1.850	1824.00
$\text{C}_2\text{H}_5\text{OH} + \text{O} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{OH}$	1.580e+07	2.000	4448.00
$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3 \rightleftharpoons \text{PC}_2\text{H}_4\text{OH} + \text{CH}_4$	2.190e+02	3.180	9622.00
$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CHOH} + \text{CH}_4$	7.280e+02	2.990	7948.00
$\text{C}_2\text{H}_5\text{OH} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{CH}_4$	1.450e+02	2.990	7649.00
$\text{C}_2\text{H}_5\text{OH} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHOH} + \text{H}_2\text{O}_2$	8.200e+03	2.550	10750.00
$\text{C}_2\text{H}_5\text{OH} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{H}_2\text{O}_2$	2.500e+12	0.000	24000.00
$\text{CH}_3\text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}$	5.430e+15	-0.690	22230.00
$\text{CH}_3\text{CH}_2\text{O} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{O}$	1.320e+20	-2.020	20750.00
$\text{CH}_3\text{CH}_2\text{O} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{HO}_2$	4.000e+10	0.000	1100.00
$\text{CH}_3\text{CH}_2\text{O} + \text{CO} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO}_2$	4.680e+02	3.160	5380.00
$\text{CH}_3\text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CH}_2\text{O} + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O}$	1.000e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_3\text{CHOH} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{HO}_2$	1.000e+13	0.000	5569.00
$\text{CH}_3\text{CHOH} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_6 + \text{H}_2\text{O}$	1.000e+13	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{O} \rightleftharpoons \text{CH}_3\text{CHO} + \text{OH}$	1.000e+14	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}_2\text{O}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{H} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{OH}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{OH} + \text{OH}$	4.000e+13	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H}_2\text{O}$	5.000e+12	0.000	0.00
$\text{CH}_3\text{CHOH} + \text{M} \rightleftharpoons \text{CH}_3\text{CHO} + \text{H} + \text{M}$	1.000e+14	0.000	25000.00
$\text{CH}_3\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_2\text{CHO} + \text{H}_2\text{O}$	3.370e+11	0.000	-620.00
$\text{CH}_3\text{CHO} + \text{O} \rightleftharpoons \text{CH}_2\text{CHO} + \text{OH}$	3.720e+13	-0.200	3556.00
$\text{CH}_3\text{CHO} + \text{H} \rightleftharpoons \text{CH}_2\text{CHO} + \text{H}_2$	2.720e+03	3.100	5210.00
$\text{CH}_3\text{CHO} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{CHO} + \text{CH}_4$	2.450e+01	3.150	5727.00
$\text{C}_2\text{H}_5\text{OCHO} + \text{H} \rightleftharpoons \text{C}_2\text{H}_5\text{OCO} + \text{H}_2$	6.500e+05	2.400	4471.00
$\text{C}_2\text{H}_5\text{OCHO} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{OCO} + \text{H}_2\text{O}$	2.340e+07	1.610	-35.00
$\text{C}_2\text{H}_5\text{OCHO} + \text{M} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{HCO} + \text{M}$	4.380e+16	0.000	98919.00
$\text{C}_2\text{H}_5\text{OCO} + \text{M} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{CO} + \text{M}$	8.640e+15	0.000	14400.00
$\text{C}_2\text{H}_5\text{OCH}_2 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_2\text{O}$	1.270e+14	-0.220	27200.00
$\text{C}_2\text{H}_4 + \text{OH} \rightleftharpoons \text{PC}_2\text{H}_4\text{OH}$	1.000e+26	-4.447	3720.00
$\text{PC}_2\text{H}_4\text{OH} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{OH}$	1.810e+12	0.000	0.00
$\text{PC}_2\text{H}_4\text{OH} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{O} + \text{H}_2\text{O}$	1.000e+13	0.000	0.00
$\text{CH}_3\text{CO} + \text{M} \rightleftharpoons \text{CH}_3 + \text{CO} + \text{M}$	2.000e+13	0.000	17087.00
$\text{C}_2\text{H}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CHO} + \text{O}$	1.080e+13	-0.610	5260.00
$\text{CH}_2\text{CHO} \rightleftharpoons \text{CH}_3 + \text{CO}$	1.170e+43	-9.830	43756.00
$\text{H} + \text{CH}_2\text{CO} (+\text{M}) \rightleftharpoons \text{CH}_2\text{CHO} (+\text{M})$	4.865e+11	0.422	-1755.00
Low pressure limit	1.012e+42	-7.630	3854.00
Troe parameters: a=0.465, T***=201, T*=1773, T**=5333			
<i>Enhanced Collision. Efficiencies:</i> H ₂ = 2, H ₂ O = 6, CH ₄ = 2			
CO = 1.5, CO ₂ = 2, C ₂ H ₆ = 3, AR = 0.7			
$\text{CH}_2\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{HO}_2$	1.580e+10	0.000	0.00
$\text{CH}_2\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CO} + \text{OH}$	2.510e+10	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2\text{CHO} + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{HCO}$	3.980e+13	0.000	0.00
$\text{CH}_2\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2\text{O}$	2.000e+13	0.000	0.00
$\text{CH}_2\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{HCO} + \text{OH}$	1.100e+13	0.000	0.00
$\text{C}_2\text{H}_5 + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_8$	3.370e+13	0.000	0.00
$\text{C}_5\text{H}_5 + \text{H} \rightleftharpoons \text{C}_5\text{H}_6$	2.710e+63	-14.790	21050.00
$\text{CH}_2\text{O} + \text{HO}_2 \rightleftharpoons \text{HCO} + \text{H}_2\text{O}_2$	3.010e+12	0.000	13076.00
$\text{CH}_2\text{O} + \text{O}_2 \rightleftharpoons \text{HO}_2 + \text{HCO}$	1.000e+14	0.000	40000.00
$\text{CH}_2\text{O} + \text{M} \rightleftharpoons \text{CO} + \text{H}_2 + \text{M}$	2.500e+14	0.000	28215.00
$\text{H}_2\text{O}_2 + \text{H} \rightleftharpoons \text{OH} + \text{H}_2\text{O}$	2.410e+13	0.000	3974.00
$\text{H}_2\text{O}_2 + \text{O} \rightleftharpoons \text{OH} + \text{HO}_2$	9.550e+06	2.000	3970.00
$\text{HCO} + \text{HO}_2 \rightleftharpoons \text{CO}_2 + \text{OH} + \text{H}$	3.000e+13	0.000	0.00
$\text{H} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O} + \text{O}$	3.010e+13	0.000	1721.00
$\text{CH}_2\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{HCO}$	3.010e+13	0.000	0.00
$\text{CH}_3\text{CHO} + \text{H} \rightleftharpoons \text{CH}_3\text{CO} + \text{H}_2$	3.600e+14	0.000	7000.00
$\text{CH}_3\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CO} + \text{H}_2\text{O}_2$	3.000e+12	0.000	11900.00
$\text{CH}_3\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{CHO} + \text{H}_2\text{O}_2$	1.000e+12	0.000	14000.00
$\text{CH}_2\text{CHO} + \text{H} \rightleftharpoons \text{CH}_3 + \text{HCO}$	2.200e+13	0.000	0.00
$\text{CH}_2\text{CHO} + \text{H} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2$	1.100e+13	0.000	0.00
$\text{CH}_2\text{CHO} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO} + \text{H}$	4.900e+14	-0.500	0.00
$\text{CH}_2\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{O}_2$	3.000e+12	0.000	0.00
$\text{CH}_2\text{CO} + \text{O} \rightleftharpoons \text{CO}_2 + \text{CH}_2$	1.750e+12	0.000	1350.00
$\text{CH}_2\text{CO} + \text{O} \rightleftharpoons \text{HCCO} + \text{OH}$	1.000e+13	0.000	8000.00
$\text{CH} + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}$	9.460e+13	0.000	-515.00
$\text{CH} + \text{CO} (+ \text{M}) \rightleftharpoons \text{HCCO} (+ \text{M})$	5.000e+13	0.000	0.00
<i>Enhanced Collision. Efficiencies: $\text{H}_2 = 2$, $\text{H}_2\text{O} = 6$, $\text{CH}_4 = 2$</i>			
<i>$\text{CO} = 1.5$, $\text{CO}_2 = 2$, $\text{C}_2\text{H}_6 = 3$, $\text{Ar} = 0.7$</i>			
Low pressure limit	2.690e+28	-3.740	1936.00
<i>Troe parameters: $a=0.5757$, $T^{***}=237$, $T^*=1652$, $T^{**}=5069$</i>			
$\text{HCCO} + \text{CH}_2 \rightleftharpoons \text{C}_2\text{H}_3 + \text{CO}$	3.000e+13	0.000	0.00
$\text{CH}_3\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_3 + \text{HOCHO}$	3.000e+15	-1.076	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2\text{O} + \text{OH} \rightleftharpoons \text{HOCHO} + \text{H}$	2.620e+06	2.060	916.00
$\text{CH}_2\text{O} + \text{OCHO} \rightleftharpoons \text{HOCHO} + \text{HCO}$	5.060e+12	0.000	13600.00
$\text{HOCHO} + \text{M} \rightleftharpoons \text{CO} + \text{H}_2\text{O} + \text{M}$	2.090e+14	0.000	40400.00
$\text{HOCHO} + \text{M} \rightleftharpoons \text{CO}_2 + \text{H}_2 + \text{M}$	1.350e+15	0.000	60600.00
$\text{HOCHO} + \text{OH} \rightleftharpoons \text{CO} + \text{H}_2\text{O} + \text{OH}$	1.850e+07	1.510	-962.00
$\text{HOCHO} + \text{OH} \rightleftharpoons \text{CO}_2 + \text{H}_2\text{O} + \text{H}$	2.620e+06	2.060	916.00
$\text{HOCHO} + \text{H} \rightleftharpoons \text{CO}_2 + \text{H}_2 + \text{H}$	4.240e+06	2.100	4868.00
$\text{HOCHO} + \text{H} \rightleftharpoons \text{CO} + \text{H}_2 + \text{OH}$	6.060e+13	-0.350	2988.00
$\text{HOCHO} + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{CO} + \text{OH}$	3.900e-07	5.800	2200.00
$\text{HOCHO} + \text{O} \rightleftharpoons \text{CO} + \text{OH} + \text{OH}$	1.770e+18	-1.900	2975.00
$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_4 + \text{CO}_2$	7.080e+13	0.000	74600.00
$\text{CH}_3\text{COOH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2\text{O}$	4.470e+14	0.000	79800.00
$\text{CH}_3\text{CO}_2 + \text{M} \rightleftharpoons \text{CH}_3 + \text{CO}_2 + \text{M}$	8.700e+15	0.000	14400.00
$\text{CH}_3\text{COOH} + \text{H} \rightleftharpoons \text{CH}_2\text{COOH} + \text{H}_2$	6.660e+05	2.540	6754.00
$\text{CH}_3\text{COOH} + \text{O} \rightleftharpoons \text{CH}_2\text{COOH} + \text{OH}$	9.810e+05	2.430	4750.00
$\text{CH}_3\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_2\text{COOH} + \text{H}_2\text{O}$	5.280e+09	0.970	1586.00
$\text{CH}_3\text{COOH} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{COOH} + \text{H}_2\text{O}_2$	5.610e+12	0.000	19426.00
$\text{CH}_2\text{COOH} \rightleftharpoons \text{CH}_2\text{CO} + \text{OH}$	4.000e+13	0.000	29075.00
$\text{CH}_3\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}$	2.810e+02	2.970	-580.00
$\text{CH}_3\text{COOH} + \text{H} \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{H}_2$	1.500e+07	1.600	3038.00
$\text{CH}_3\text{COOH} + \text{O} \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{OH}$	1.580e+07	2.000	4448.00
$\text{CH}_3\text{COOH} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{CH}_4$	1.450e+02	2.990	7649.00
$\text{CH}_3\text{COOH} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{H}_2\text{O}_2$	2.500e+12	0.000	24000.00
$\text{O}_2 + \text{CH}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{O}$	6.000e+12	0.000	0.00
$\text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{C}_2\text{H}_5 + \text{HCO}$	2.450e+15	0.000	72864.50
$\text{H} + \text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{H}_2 + \text{C}_2\text{H}_5\text{CO}$	1.200e+14	0.000	7000.00
$\text{O} + \text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{OH} + \text{C}_2\text{H}_5\text{CO}$	5.850e+12	0.000	1808.00
$\text{HO}_2 + \text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{H}_2\text{O}_2 + \text{C}_2\text{H}_5\text{CO}$	2.800e+12	0.000	13600.00
$\text{C}_2\text{H}_5\text{CO} + \text{M} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO} + \text{M}$	8.640e+15	0.000	14400.00
$\text{CH}_3\text{CO} + \text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{HCO}$	1.710e+11	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_3\text{COCH}_3 + \text{H} \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{H}_2$	1.440e+09	1.500	7410.00
$\text{CH}_3\text{COCH}_3 + \text{O} \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{OH}$	1.000e+13	0.000	5950.00
$\text{CH}_3\text{COCH}_3 + \text{OH} \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$	8.000e+10	0.000	0.00
Duplicate Reaction			
$\text{CH}_3\text{COCH}_3 + \text{OH} \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}$	6.080e+08	1.410	2560.00
Duplicate Reaction			
$\text{CH}_3\text{COCH}_3 + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{CH}_4$	9.500e+03	2.500	8385.00
$\text{CH}_3\text{COCH}_3 (+\text{M}) \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_3 (+\text{M})$	7.108e+21	-1.570	84680.00
Low pressure limit	7.013e+89	-20.380	107150.00
Troe parameters: a=0.863034, T***=9.99954E+009			
T*=416.4, T**=3.2899E+009			
$\text{CH}_3\text{COCH}_2 + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{HCO}$	6.310e+11	0.000	8500.00
$\text{CH}_3\text{COCH}_2 + \text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{CH}_3\text{CO}$	6.310e+11	0.000	8500.00
$\text{CH}_3\text{COCH}_2 + \text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{C}_2\text{H}_5\text{CO}$	3.160e+11	0.000	7593.00
$\text{CH}_3\text{COCH}_3 + \text{CH}_3 \rightleftharpoons \text{CH}_3 + \text{CH}_4 + \text{CH}_2\text{CO}$	4.000e+11	0.000	9682.00
$\text{CH}_3\text{COCH}_3 + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CO} + \text{C}_2\text{H}_6$	7.940e+10	0.000	5989.00
$\text{CH}_3\text{COCH}_3 + \text{O} \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_3\text{O}$	5.010e+12	0.000	1796.00
$\text{CH}_3\text{COCH}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3$	1.000e+13	0.000	28000.00
$\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{CH}_3\text{OH}$	4.340e+11	0.000	6460.00
$\text{CH}_3\text{COCH}_3 + \text{O}_2 \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{HO}_2$	6.030e+13	0.000	48500.00
$\text{CH}_3\text{COCH}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{H}_2\text{O}_2$	1.700e+13	0.000	20460.00
$\text{CH}_3 + \text{O}_2 (+\text{M}) \rightleftharpoons \text{CH}_3\text{O}_2 (+\text{M})$	1.006e+08	1.630	0.00
Low pressure limit	3.816e+31	-4.890	3432.00
Troe parameters: a=0.045, T***=880.1			
T*=2.5E+009, T**=1.786E+009			
$\text{CH}_3\text{O}_2 + \text{CH}_2\text{O} \rightleftharpoons \text{CH}_3\text{O}_2\text{H} + \text{HCO}$	1.990e+12	0.000	11670.00
$\text{CH}_4 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_3 + \text{CH}_3\text{O}_2\text{H}$	1.810e+11	0.000	18480.00
$\text{CH}_3\text{OH} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_2\text{OH} + \text{CH}_3\text{O}_2\text{H}$	1.810e+12	0.000	13710.00
$\text{CH}_3\text{O}_2 + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{O} + \text{CH}_3\text{O}$	9.000e+12	0.000	-1200.00
$\text{CH}_3\text{O}_2 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{O}_2\text{H} + \text{O}_2$	2.470e+11	0.000	-1570.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_3\text{OH} + \text{O}_2$	3.110e+14	-1.610	-1051.00
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{O}_2 + \text{CH}_3\text{O} + \text{CH}_3\text{O}$	1.400e+16	-1.610	1860.00
$\text{CH}_3\text{O}_2 + \text{H} \rightleftharpoons \text{CH}_3\text{O} + \text{OH}$	9.600e+13	0.000	0.00
$\text{CH}_3\text{O}_2 + \text{O} \rightleftharpoons \text{CH}_3\text{O} + \text{O}_2$	3.600e+13	0.000	0.00
$\text{CH}_3\text{O}_2 + \text{OH} \rightleftharpoons \text{CH}_3\text{OH} + \text{O}_2$	6.000e+13	0.000	0.00
$\text{H}_2 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{H} + \text{CH}_3\text{O}_2\text{H}$	1.500e+14	0.000	26030.00
$\text{CH}_3\text{O}_2 + \text{CH}_3\text{CHO} \rightleftharpoons \text{CH}_3\text{O}_2\text{H} + \text{CH}_3\text{CO}$	3.010e+12	0.000	11930.00
$\text{CH}_3\text{COCH}_3 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_3\text{COCH}_2 + \text{CH}_3\text{O}_2\text{H}$	1.700e+13	0.000	20460.00
$\text{OH} + \text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{H}_2\text{O} + \text{C}_2\text{H}_5\text{CO}$	2.650e+12	0.000	-730.00
$\text{C}_2\text{H}_5\text{CHO} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{CO} + \text{CH}_4$	2.608e+06	1.780	5911.00
$\text{C}_2\text{H}_5\text{CHO} + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{CO} + \text{HO}_2$	2.000e+13	0.500	42200.00
$\text{C}_2\text{H}_5\text{CHO} + \text{H} \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{H}_2$	1.300e+06	2.400	4471.00
$\text{C}_2\text{H}_5\text{CHO} + \text{O} \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{OH}$	4.770e+04	2.710	2106.00
$\text{C}_2\text{H}_5\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{H}_2\text{O}$	4.680e+07	1.610	-35.00
$\text{C}_2\text{H}_5\text{CHO} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{CH}_4$	9.993e+10	0.000	8323.28
$\text{C}_2\text{H}_5\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{H}_2\text{O}_2$	1.000e+12	0.000	12000.00
$\text{C}_2\text{H}_5\text{CHO} + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{CH}_3\text{OH}$	1.017e+11	0.000	2979.08
$\text{C}_2\text{H}_5\text{CHO} + \text{H} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2$	9.500e+04	2.750	6280.00
$\text{C}_2\text{H}_5\text{CHO} + \text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{OH}$	9.500e+04	2.680	3716.00
$\text{C}_2\text{H}_5\text{CHO} + \text{OH} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O}$	5.250e+09	0.970	1590.00
$\text{C}_2\text{H}_5\text{CHO} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{CH}_4$	1.258e+11	0.000	12733.37
$\text{C}_2\text{H}_5\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{H}_2\text{O}_2$	9.993e+11	0.000	13994.76
$\text{C}_2\text{H}_5\text{CHO} + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{CH}_3\text{OH}$	2.408e+11	0.000	7090.55
$\text{CH}_3\text{CHCHO} \rightleftharpoons \text{CH}_2\text{CHCHO} + \text{H}$	4.164e+12	-0.020	34210.00
$\text{CH}_2\text{CH}_2\text{CHO} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HCO}$	1.260e+13	0.000	30340.30
$\text{CH}_2\text{CH}_2\text{CHO} \rightleftharpoons \text{CH}_2\text{CHCHO} + \text{H}$	1.670e+13	0.000	46222.00
$\text{CH}_2\text{CH}_2\text{CHO} \rightleftharpoons \text{CH}_3\text{CHCHO}$	2.000e+12	0.000	36790.60
$\text{CH}_3\text{CHCO} \rightleftharpoons \text{CH}_3 + \text{HCCO}$	1.170e+16	0.000	85765.10
$\text{CH}_3\text{CHCO} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CO}$	3.000e+14	0.000	70953.30
$\text{CH}_2\text{CHCHO} \rightleftharpoons \text{C}_2\text{H}_3 + \text{HCO}$	2.450e+16	0.000	84128.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_3\text{CHCO} + \text{H} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO}$	4.400e+12	0.000	1459.00
$\text{C}_2\text{H}_5\text{CHO} + \text{M} \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{H} + \text{M}$	5.000e+15	0.000	94990.00
$\text{C}_2\text{H}_5\text{CHO} + \text{M} \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{H} + \text{M}$	8.000e+15	0.000	98000.00
$\text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{CH}_3 + \text{CH}_2\text{CHO}$	7.000e+15	0.000	81703.00
$\text{C}_2\text{H}_5\text{CHO} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CH}_2\text{O}$	5.130e+13	0.000	63063.00
$\text{C}_2\text{H}_5\text{CHO} + \text{M} \rightleftharpoons \text{C}_2\text{H}_5\text{CO} + \text{H} + \text{M}$	8.000e+15	0.000	87676.00
$\text{C}_2\text{H}_5\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CHCHO} + \text{HO}_2$	4.000e+13	0.000	47690.00
$\text{C}_2\text{H}_5\text{CHO} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CH}_2\text{CHO} + \text{HO}_2$	4.000e+13	0.000	50870.00
$\text{C}_2\text{H}_5\text{CO} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3$	2.745e+09	1.410	35830.00
$\text{CH}_3\text{CHCHO} \rightleftharpoons \text{CH}_3\text{CHCO} + \text{H}$	1.345e+13	-0.170	33460.00
$\text{CH}_3\text{CHCHO} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{OH}$	9.640e+12	0.000	0.00
$\text{CH}_3\text{CHOCHO} \rightleftharpoons \text{CH}_3\text{CHO} + \text{HCO}$	3.980e+13	0.000	9700.00
$\text{CH}_3\text{CHCO} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO}_2$	1.730e+12	0.000	-1010.00
$\text{CH}_3\text{CHCO} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHOH} + \text{CO}$	2.000e+12	0.000	-1010.00
$\text{CH}_3\text{CHCO} + \text{O} \rightleftharpoons \text{CH}_3\text{CHO} + \text{CO}$	3.200e+12	0.000	-437.00
$\text{CH}_2\text{CHCHO} + \text{H} \rightleftharpoons \text{H}_2 + \text{CH}_2\text{CHCO}$	4.000e+13	0.000	4200.00
$\text{CH}_2\text{CHCHO} + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CH}_2\text{CHCO}$	4.200e+12	0.000	500.00
$\text{CH}_2\text{CHCHO} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{CH}_2\text{CHCO}$	2.800e+12	0.000	13600.00
$\text{CH}_2\text{CHCHO} + \text{O} \rightleftharpoons \text{OH} + \text{CH}_2\text{CHCO}$	5.010e+12	0.000	1790.00
$\text{CH}_2\text{CHCO} + \text{M} \rightleftharpoons \text{C}_2\text{H}_3 + \text{CO} + \text{M}$	8.600e+15	0.000	23000.00
<i>Enhanced Collision. Efficiencies:</i> $\text{H}_2\text{O} = 16.25$, $\text{CH}_4 = 16.25$, $\text{CO} = 1.875$			
$\text{CO}_2 = 3.75$, $\text{C}_2\text{H}_6 = 16.25$			
$\text{CH}_2\text{CHCO} + \text{HO}_2 \rightleftharpoons \text{C}_2\text{H}_3 + \text{CO}_2 + \text{OH}$	2.000e+13	0.000	0.00
$\text{C}_2\text{H}_5 + \text{H} (+ \text{M}) \rightleftharpoons \text{C}_2\text{H}_6 (+ \text{M})$	5.210e+17	-0.990	1580.00
Low pressure limit	1.990e+41	-7.080	6685.00
Troe parameters: $a=0.8422$, $T^{***}=125$			
$T^*=2219$, $T^{**}=6882$			
<i>Enhanced Collision. Efficiencies:</i> $\text{H}_2 = 2$, $\text{H}_2\text{O} = 6$, $\text{CH}_4 = 2$			
$\text{CO} = 1.5$, $\text{CO}_2 = 2$, $\text{C}_2\text{H}_6 = 3$, $\text{Ar} = 0.7$			
$\text{C}_2\text{H}_4 + \text{H} (+ \text{M}) \rightleftharpoons \text{C}_2\text{H}_5 (+ \text{M})$	1.367e+09	1.463	1355.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
Low pressure limit	2.027e+39	-6.642	5769.00
Troe parameters: a=1, T***=1E-015			
T*=95, T**=200			
Enhanced Collision. Efficiencies: H ₂ = 2, H ₂ O = 6, CH ₄ = 2			
CO = 1.5, CO ₂ = 2, C ₂ H ₆ = 3, Ar = 0.7			
C ₅ H ₅ + H⇌C ₅ H ₄ + H ₂	3.230e+07	2.095	15842.00
C ₅ H ₅ + OH⇌C ₅ H ₄ + H ₂ O	2.110e+13	0.000	4571.00
C ₅ H ₅ + O⇌C ₅ H ₄ + OH	2.000e+13	0.000	14694.00
C ₅ H ₅ + CH ₃ ⇌C ₅ H ₄ + CH ₄	2.000e+12	0.000	15060.00
C ₅ H ₄ H + H⇌C ₅ H ₄ + H ₂	2.800e+13	0.000	2259.00
C ₅ H ₄ H + OH⇌C ₅ H ₄ + H ₂ O	3.080e+06	2.000	0.00
C ₅ H ₄ H + O⇌C ₅ H ₄ + OH	4.770e+04	2.710	1106.00
C ₅ H ₅ ⇌C ₅ H ₄ H	5.170e+80	-20.400	96185.00
C ₅ H ₅ + O⇌C ₅ H ₄ O + H	5.810e+13	0.000	20.00
C ₅ H ₅ + OH⇌C ₅ H ₄ OH + H	9.000e+13	0.000	0.00
C ₅ H ₄ OH⇌C ₅ H ₄ O + H	2.100e+13	0.000	48000.00
C ₅ H ₄ OH + O ₂ ⇌C ₅ H ₄ O + HO ₂	3.000e+13	0.000	5000.00
C ₅ H ₄ O + H⇌NC ₄ H ₅ + CO	4.300e+09	1.450	3900.00
C ₅ H ₄ H⇌C ₃ H ₃ + C ₂ H ₂	3.400e+80	-19.200	102265.00
C ₅ H ₆ + H⇌C ₅ H ₄ H + H ₂	2.800e+13	0.000	35139.00
C ₅ H ₆ + OH⇌C ₅ H ₄ H + H ₂ O	3.080e+06	2.000	32880.00
C ₅ H ₆ + O⇌C ₅ H ₄ H + OH	4.770e+04	2.710	33986.00
C ₅ H ₆ + CH ₃ ⇌C ₅ H ₄ H + CH ₄	1.800e-01	4.000	32880.00
C ₄ H ₂ + CH ₂ ⇌C ₅ H ₃ (L) + H	1.300e+13	0.000	0.00
C ₄ H ₂ + CH ₂ (s)⇌C ₅ H ₃ (L) + H	3.000e+13	0.000	0.00
C ₅ H ₃ (L) + H⇌C ₅ H ₂ (L) + H ₂	6.030e+13	0.000	15103.00
C ₅ H ₄ + H⇌C ₅ H ₃ + H ₂	1.000e+06	2.500	5000.00
C ₅ H ₄ + OH⇌C ₅ H ₃ + H ₂ O	1.000e+06	2.000	0.00
C ₅ H ₄ + O⇌C ₅ H ₃ + OH	1.000e+06	2.500	3000.00
C ₅ H ₃ + H⇌C ₅ H ₄	1.000e+14	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_5H_3 + O_2 \rightleftharpoons C_2H_2 + HCCO + CO$	1.000e+12	0.000	0.00
$C_5H_2(L) + OH \rightleftharpoons C_4H_2 + H + CO$	2.000e+13	0.000	0.00
$C_5H_2(L) + O_2 \rightleftharpoons H_2C_4O + CO$	1.000e+12	0.000	0.00
$C_5H_3(L) + OH \rightleftharpoons C_5H_2(L) + H_2O$	1.000e+13	0.000	0.00
$C_5H_3(L) + O_2 \rightleftharpoons H_2C_4O + HCO$	1.000e+12	0.000	0.00
$C_4H_2 + CH \rightleftharpoons C_5H_2(L) + H$	5.000e+13	0.000	0.00
$C_5H_6 + O \rightleftharpoons C_5H_5O + H$	1.330e+13	-0.100	361.00
$HCCO + OH \rightleftharpoons C_2O + H_2O$	3.000e+13	0.000	0.00
$C_2O + H \rightleftharpoons CH + CO$	5.000e+13	0.000	0.00
$C_2O + O \rightleftharpoons CO + CO$	5.000e+13	0.000	0.00
$C_2O + OH \rightleftharpoons CO + CO + H$	2.000e+13	0.000	0.00
$C_2O + O_2 \rightleftharpoons CO + CO + O$	2.000e+13	0.000	0.00
$H_2C_4O + O \rightleftharpoons CH_2CO + C_2O$	2.000e+07	1.900	200.00
$CH_3CHO + CH_3 \rightleftharpoons CH_3COCH_3 + H$	1.660e+10	0.000	12400.00
$C_5H_5 \rightleftharpoons C_3H_3 + C_2H_2$	2.790e+79	-18.800	130834.00
$HCO + HCO \rightleftharpoons H_2 + CO + CO$	3.000e+12	0.000	0.00
$C_2H + H(+M) \rightleftharpoons C_2H_2(+M)$	1.000e+17	-1.000	0.00
Low pressure limit	3.750e+33	-4.800	1900.00
Troe parameters: a=0.6464, T***=132			
T*=1315, T**=5566			
$C_4H + H(+M) \rightleftharpoons C_4H_2(+M)$	1.000e+17	-1.000	0.00
Low pressure limit	3.750e+33	-4.800	1900.00
Troe parameters: a=0.6464, T***=132			
T*=1315, T**=5566			
$C_2H + C_2H \rightleftharpoons C_4H_2$	5.000e+13	0.000	0.00
$C_5H_5 + O_2 \rightleftharpoons C_5H_4O + OH$	3.440e+11	-0.010	25320.00
$C_5H_5 + O_2 \rightleftharpoons C_5H_5O + O$	7.730e+15	-0.730	48740.00
$C_5H_5 + HO_2 \rightleftharpoons C_5H_5O + OH$	6.270e+29	-4.690	11649.00
$C_5H_5 + HO_2 \rightleftharpoons C_5H_4O + H_2O$	1.190e+33	-6.520	13401.00
$C_5H_4O + O \rightleftharpoons CO + HCO + C_3H_3$	6.200e+08	1.450	-858.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2\text{CO} + \text{H} \rightleftharpoons \text{HCCO} + \text{H}_2$	3.000e+07	2.000	10000.00
$\text{CH}_2\text{CO} + \text{OH} \rightleftharpoons \text{HCCO} + \text{H}_2\text{O}$	7.500e+12	0.000	2000.00
$\text{H} + \text{CH}_2\text{CO} \rightleftharpoons \text{CH}_3 + \text{CO}$	5.930e+06	2.000	1300.00
$\text{CH}_2\text{CO} + \text{OH} \rightleftharpoons \text{CH}_2\text{OH} + \text{CO}$	2.000e+12	0.000	-1010.00
$\text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2$	9.123e+31	-6.880	33900.00
$\text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_4\text{O}_{12} + \text{OH}$	8.386e+56	-15.610	43540.00
$\text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{OH}$	5.838e+36	-9.840	37810.00
Duplicate Reaction			
$\text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{OH}$	1.135e-19	6.750	15760.00
Duplicate Reaction			
$\text{C}_2\text{H}_4\text{O}_2\text{H} \rightleftharpoons \text{C}_2\text{H}_5\text{O}_2$	5.198e+06	-0.229	7193.00
$\text{C}_2\text{H}_4\text{O}_2\text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HO}_2$	6.877e+35	-8.690	21220.00
$\text{C}_2\text{H}_4\text{O}_2\text{H} \rightleftharpoons \text{C}_2\text{H}_4\text{O}_{12} + \text{OH}$	2.684e+35	-8.290	19770.00
$\text{C}_2\text{H}_4\text{O}_2\text{H} \rightleftharpoons \text{CH}_3\text{CHO} + \text{OH}$	4.106e+22	-6.730	18980.00
$\text{C}_3\text{H}_4 - \text{P} + \text{H} \rightleftharpoons \text{C}_3\text{H}_5 - \text{A}$	2.200e+59	-13.610	34900.00
$\text{C}_3\text{H}_5 - \text{A} + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{OH}$	2.470e+13	-0.450	23017.00
$\text{C}_3\text{H}_5 - \text{A} + \text{O}_2 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{HO}_2$	2.180e+21	-2.850	30755.00
$\text{C}_3\text{H}_5 - \text{A} + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CHO} + \text{CH}_2\text{O}$	7.140e+15	-1.210	21046.00
$\text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_3\text{H}_5 - \text{t}$	6.400e+51	-12.120	75700.00
$\text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_3\text{H}_5 - \text{s}$	9.700e+48	-11.730	73700.00
$\text{C}_3\text{H}_5 - \text{t} \rightleftharpoons \text{C}_3\text{H}_5 - \text{s}$	5.100e+52	-13.370	57200.00
$\text{CH} + \text{OH} \rightleftharpoons \text{HCO} + \text{H}$	3.000e+13	0.000	0.00
$\text{CH} + \text{O} \rightleftharpoons \text{C} + \text{OH}$	1.800e+14	0.000	0.00
$\text{CH} + \text{O}_2 \rightleftharpoons \text{HCO} + \text{O}$	1.000e+13	0.000	0.00
$\text{CH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{H}$	1.710e+13	-0.000	-755.00
$\text{CH} + \text{CH}_4 \rightleftharpoons \text{C}_2\text{H}_4 + \text{H}$	6.000e+13	0.000	0.00
$\text{CH} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}$	3.000e+13	0.000	0.00
$\text{C}_2\text{H}_4\text{O}_{12} \rightleftharpoons \text{CH}_4 + \text{CO}$	1.210e+13	0.000	57200.00
$\text{C}_2\text{H}_4\text{O}_{12} + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{HO}_2$	4.000e+13	0.000	61500.00
$\text{C}_2\text{H}_4\text{O}_{12} + \text{H} \rightleftharpoons \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	5.000e+09	0.000	5000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_2H_4O_{12} + H \rightleftharpoons C_2H_4 + OH$	9.510e+10	0.000	5000.00
$C_2H_4O_{12} + O \rightleftharpoons C_2H_3O_{12} + OH$	1.910e+12	0.000	5250.00
$C_2H_5O_2 + H_2O_2 \rightleftharpoons C_2H_5O_2H + HO_2$	2.410e+12	0.000	9936.00
$C_2H_5O_2 + CH_3 \rightleftharpoons CH_3CH_2O + CH_3O$	8.170e+12	0.000	-906.00
$C_2H_5O_2 + HO_2 \rightleftharpoons C_2H_5O_2H + O_2$	3.400e+11	0.000	-1300.00
$C_2H_5O_2 + CH_2O \rightleftharpoons C_2H_5O_2H + HCO$	1.990e+12	0.000	11660.00
$C_2H_4 + C_2H_5O_2 \rightleftharpoons C_2H_3 + C_2H_5O_2H$	2.230e+12	0.000	17190.00
$CH_4 + C_2H_5O_2 \rightleftharpoons CH_3 + C_2H_5O_2H$	1.810e+11	0.000	18480.00
$CH_3OH + C_2H_5O_2 \rightleftharpoons CH_2OH + C_2H_5O_2H$	1.810e+12	0.000	13710.00
$C_3H_6 + C_2H_5O_2 \rightleftharpoons C_3H_5 + A + C_2H_5O_2H$	3.240e+11	0.000	14900.00
$C_2H_5O_2 + C_3H_8 \rightleftharpoons C_2H_5O_2H + NC_3H_7$	1.700e+13	0.000	20460.00
$C_2H_5O_2 + C_3H_8 \rightleftharpoons C_2H_5O_2H + iC_3H_7$	2.000e+12	0.000	17000.00
$C_4H_8 - 1 + C_2H_5O_2 \rightleftharpoons C_4H_7 - 3 + C_2H_5O_2H$	1.400e+12	0.000	14900.00
$C_2H_5O_2 + C_2H_5O_2 \rightleftharpoons CH_3CH_2O + CH_3CH_2O + O_2$	1.400e+16	-1.610	1860.00
$C_2H_5O_2H + O \rightleftharpoons OH + C_2H_5O_2$	2.000e+13	0.000	4750.00
$C_2H_5O_2H + OH \rightleftharpoons C_2H_5O_2 + H_2O$	2.000e+12	0.000	-370.00
$C_2H_5O_2H + H \rightleftharpoons CH_3CHO + OH + H_2$	3.200e+13	0.000	7700.00
$C_2H_5O_2H + CH_3 \rightleftharpoons CH_3CHO + OH + CH_4$	5.700e+11	0.000	8700.00
$C_2H_5O_2H + C_2H_5 \rightleftharpoons CH_3CHO + OH + C_2H_6$	3.400e+11	0.000	11400.00
$C_2H_5O_2H + OH \rightleftharpoons CH_3CHO + OH + H_2O$	5.900e+12	0.000	900.00
$C_2H_5O_2H + HCO \rightleftharpoons CH_3CHO + OH + CH_2O$	1.800e+12	0.000	16700.00
$C_2H_5O_2H + CH_3O \rightleftharpoons CH_3CHO + OH + CH_3OH$	6.300e+11	0.000	5500.00
$C_2H_5O_2H + HO_2 \rightleftharpoons CH_3CHO + OH + H_2O_2$	8.000e+11	0.000	16200.00
$CHOCHO(+ M) \rightleftharpoons CH_2O + CO(+ M)$	4.270e+12	0.000	50600.00
Low pressure limit	8.910e+16	0.000	49200.00
$CHOCHO(+ M) \rightleftharpoons CO + CO + H_2(+ M)$	1.072e+14	0.000	55100.00
Low pressure limit	2.570e+16	0.000	38400.00
$CHOCHO + OH \rightleftharpoons CHOCO + H_2O$	1.000e+13	0.000	0.00
$CHOCHO + O \rightleftharpoons CHOCO + OH$	7.240e+12	0.000	1970.00
$CHOCHO + H \rightleftharpoons CH_2O + HCO$	1.000e+12	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CHOCHO} + \text{HO}_2 \rightleftharpoons \text{CHOCO} + \text{H}_2\text{O}_2$	1.700e+12	0.000	10700.00
$\text{CHOCHO} + \text{CH}_3 \rightleftharpoons \text{CHOCO} + \text{CH}_4$	1.740e+12	0.000	8440.00
$\text{CHOCHO} + \text{O}_2 \rightleftharpoons \text{HCO} + \text{CO} + \text{HO}_2$	6.300e+13	0.000	30000.00
$\text{HCO} + \text{HCO} \rightleftharpoons \text{CHOCHO}$	1.000e+13	0.000	0.00
$\text{CHOCO} \rightleftharpoons \text{HCO} + \text{CO}$	2.000e+07	0.000	0.00
$\text{CHOCO} + \text{O}_2 \rightleftharpoons \text{CO} + \text{CO} + \text{HO}_2$	3.980e+12	0.000	30000.00
$\text{C}_2\text{H}_3\text{O}_{12} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}$	4.960e+13	0.000	14860.00
$\text{C}_2\text{H}_3\text{O}_{12} \rightleftharpoons \text{CH}_3 + \text{CO}$	7.310e+12	0.000	14280.00
$\text{C}_2\text{H}_3\text{O}_{12} \rightleftharpoons \text{CH}_3\text{CO}$	8.511e+14	0.000	14000.00
$\text{C}_2\text{H}_3\text{O}_{12} \rightleftharpoons \text{CH}_2\text{CHO}$	8.740e+31	-6.900	14990.00
$\text{C}_2\text{H}_2\text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}$	5.000e+15	0.000	28000.00
$\text{C}_2\text{H}_2\text{OH} + \text{H} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2$	2.000e+13	0.000	4000.00
$\text{C}_2\text{H}_2\text{OH} + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{OH}$	2.000e+13	0.000	4000.00
$\text{C}_2\text{H}_2\text{OH} + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2\text{O}$	1.000e+13	0.000	2000.00
$\text{C}_2\text{H}_2\text{OH} + \text{O}_2 \rightleftharpoons \text{HCO} + \text{CO}_2 + \text{H}_2$	4.000e+12	0.000	-250.00
$\text{CH}_3\text{CO} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CO}_3$	1.200e+11	0.000	-1100.00
$\text{CH}_3\text{CO}_3 + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CO}_3\text{H} + \text{O}_2$	1.750e+10	0.000	-3275.00
$\text{CH}_3\text{CO}_3\text{H} \rightleftharpoons \text{CH}_3\text{CO}_2 + \text{OH}$	5.010e+14	0.000	40150.00
$\text{CH}_3\text{CO}_3 \rightleftharpoons \text{CH}_2\text{CO} + \text{HO}_2$	3.345e+09	1.000	32500.00
$\text{C}_2 + \text{O}_2 \rightleftharpoons \text{CO} + \text{CO}$	5.000e+13	0.000	0.00
$\text{C}_2 + \text{OH} \rightleftharpoons \text{C}_2\text{O} + \text{H}$	5.000e+13	0.000	0.00
$\text{C}_2 + \text{H}_2 \rightleftharpoons \text{C}_2\text{H} + \text{H}$	4.000e+05	2.400	1000.00
$\text{OCHO} + \text{CO} \rightleftharpoons \text{CHOOCO}$	1.500e+11	0.000	3000.00
$\text{HCO} + \text{CO}_2 \rightleftharpoons \text{CHOOCO}$	1.500e+11	0.000	36730.00
$\text{C}_3\text{H}_6 + \text{H} (+ \text{M}) \rightleftharpoons \text{NC}_3\text{H}_7 (+ \text{M})$	1.330e+13	0.000	3260.70
Low pressure limit	6.260e+38	-6.660	7000.00
Troie parameters: a=1, T***=1000			
T*=1310, T**=48097			
$\text{NC}_3\text{H}_7\text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{CHO} + \text{H}$	2.510e+14	0.000	23400.00
$\text{NC}_3\text{H}_7\text{O} + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{CHO} + \text{HO}_2$	9.090e+09	0.000	390.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2\text{O} + \text{C}_2\text{H}_5 \rightleftharpoons \text{NC}_3\text{H}_7\text{O}$	1.500e+11	0.000	11900.00
$\text{iC}_3\text{H}_7\text{O} \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{H}$	2.000e+14	0.000	21500.00
$\text{iC}_3\text{H}_7\text{O} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{COCH}_3 + \text{HO}_2$	9.090e+09	0.000	390.00
$\text{CH}_3\text{CHO} + \text{CH}_3 \rightleftharpoons \text{iC}_3\text{H}_7\text{O}$	1.500e+11	0.000	11900.00
$\text{C}_3\text{H}_5 - \text{s} + \text{CH}_2\text{O} \rightleftharpoons \text{C}_3\text{H}_6 + \text{HCO}$	5.420e+03	2.810	5862.00
$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{C}_2\text{H}_4$	2.210e+00	3.500	4682.00
$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_5 - \text{t} + \text{C}_2\text{H}_4$	2.210e+00	3.500	4682.00
$\text{C}_3\text{H}_6 + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_5 - \text{s} + \text{C}_2\text{H}_4$	2.210e+00	3.500	4682.00
$\text{C}_3\text{H}_6 + \text{OH} \rightleftharpoons \text{C}_3\text{H}_6\text{OH}$	9.930e+11	0.000	-960.00
$\text{C}_3\text{H}_5 - \text{A} + \text{HO}_2 \rightleftharpoons \text{C}_3\text{H}_5\text{O} + \text{OH}$	4.500e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{H} \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{H}_2$	6.030e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{CH}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{CH}_2 \rightleftharpoons \text{C}_4\text{H}_6 + \text{H}$	3.000e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_6$	4.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_4$	1.000e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{H}$	6.030e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{HCO} \rightleftharpoons \text{C}_3\text{H}_6 + \text{CO}$	6.030e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{CH}_2\text{O} \rightleftharpoons \text{C}_3\text{H}_6 + \text{HCO}$	1.260e+08	1.900	18180.00
$\text{C}_3\text{H}_5 - \text{A} + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_6 + \text{C}_2\text{H}_2$	4.820e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{A} + \text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_3\text{H}_6$	8.430e+10	0.000	-260.00
$\text{C}_3\text{H}_5 - \text{A} + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_3\text{H}_6$	4.000e+11	0.000	0.00
<i>Enhanced Collision. Efficiencies: REV = 6.937E+016, -1.33 = 52800</i>			
$\text{C}_3\text{H}_5 - \text{s} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{HCO}$	4.600e+16	-1.390	1010.00
$\text{C}_3\text{H}_5 - \text{s} + \text{H} \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{H}_2$	3.333e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{s} + \text{H} \rightleftharpoons \text{C}_3\text{H}_4 - \text{P} + \text{H}_2$	4.000e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{s} + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3$	1.807e+14	0.000	0.00
$\text{C}_3\text{H}_5 - \text{s} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{CH}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{s} + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_6$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{s} + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{O}_2 \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_2\text{O}$	4.600e+16	-1.390	1010.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_3\text{H}_5 - \text{t} + \text{HO}_2 \Rightarrow \text{CH}_2\text{CO} + \text{CH}_3 + \text{OH}$	4.500e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{O} \Rightarrow \text{CH}_2\text{CO} + \text{CH}_3$	6.000e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{HCO} \Rightarrow \text{CO} + \text{C}_3\text{H}_6$	9.000e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{OH} \Rightarrow \text{CH}_2\text{CO} + \text{CH}_3 + \text{H}$	5.000e+12	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{H} \rightleftharpoons \text{C}_3\text{H}_4 - \text{P} + \text{H}_2$	1.000e+13	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{CH}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_6$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_5 - \text{t} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_4 - \text{P} + \text{CH}_4$	1.000e+11	0.000	0.00
$\text{C}_3\text{H}_4 - \text{A} + \text{HO}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2\text{O}_2$	1.800e+13	0.000	19000.00
$\text{C}_3\text{H}_4 - \text{A} + \text{HO}_2 \Rightarrow \text{CH}_2\text{CO} + \text{CH}_2 + \text{OH}$	5.000e+11	0.000	19000.00
$\text{C}_3\text{H}_4 - \text{A} + \text{HO}_2 \Rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{OH}$	5.000e+11	0.000	19000.00
$\text{C}_3\text{H}_4 - \text{A} + \text{HO}_2 \Rightarrow \text{C}_2\text{H}_2 + \text{CH}_2\text{O} + \text{OH}$	5.000e+11	0.000	19000.00
$\text{C}_3\text{H}_4 - \text{A} + \text{OH} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2\text{O}$	2.150e+12	0.000	-200.00
$\text{C}_3\text{H}_4 - \text{A} + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3$	1.000e+12	0.000	-393.00
$\text{C}_3\text{H}_4 - \text{A} + \text{OH} \rightleftharpoons \text{HCO} + \text{C}_2\text{H}_4$	1.250e+11	0.000	-393.00
$\text{C}_3\text{H}_4 - \text{A} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CO}$	1.875e+11	0.000	-393.00
$\text{C}_3\text{H}_4 - \text{A} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{H}$	3.750e+11	0.000	-393.00
$\text{C}_3\text{H}_4 - \text{A} + \text{O} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CO}$	1.125e-02	4.613	-4243.00
$\text{C}_3\text{H}_4 - \text{A} + \text{O} \rightleftharpoons \text{C}_2\text{H}_3 + \text{HCO}$	5.000e-04	4.613	-4243.00
$\text{C}_3\text{H}_4 - \text{A} + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_2$	1.000e-03	4.613	-4243.00
$\text{C}_3\text{H}_4 - \text{A} + \text{O} \rightleftharpoons \text{C}_2\text{H}_2 + \text{CH}_2\text{O}$	2.500e-03	4.613	-4243.00
$\text{C}_3\text{H}_4 - \text{A} + \text{H} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2$	1.000e+14	0.000	15009.00
$\text{C}_3\text{H}_4 - \text{A} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_3 + \text{CH}_4$	1.333e+12	0.000	7700.00
$\text{C}_3\text{H}_4 - \text{A} + \text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_3\text{H}_6$	9.000e+11	0.000	7700.00
$\text{C}_3\text{H}_4 - \text{A} + \text{C}_2\text{H} \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_2\text{H}_2$	1.000e+13	0.000	0.00
<i>Enhanced Collision. Efficiencies: REV = 1.42E+016, -1.38 = 53820</i>			
$\text{C}_3\text{H}_4\text{O} \Rightarrow \text{C}_2\text{H}_3\text{CHO}$	2.450e+14	0.000	58485.00
$\text{C}_3\text{H}_4\text{O} + \text{O}_2 \Rightarrow \text{C}_3\text{H}_3\text{O} + \text{HO}_2$	4.000e+13	0.000	61500.00
$\text{C}_3\text{H}_4\text{O} + \text{HO}_2 \Rightarrow \text{CH}_2\text{CO} + \text{CH}_2\text{O} + \text{OH}$	1.000e+12	0.000	14340.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_3\text{H}_4\text{O} + \text{HO}_2 \Rightarrow \text{C}_3\text{H}_3\text{O} + \text{H}_2\text{O}_2$	4.000e+12	0.000	17000.00
$\text{C}_3\text{H}_4\text{O} + \text{OH} \Rightarrow \text{C}_3\text{H}_3\text{O} + \text{H}_2\text{O}$	4.790e+13	0.000	5955.00
$\text{C}_3\text{H}_4\text{O} + \text{H} \Rightarrow \text{C}_3\text{H}_3\text{O} + \text{H}_2$	2.000e+13	0.000	8300.00
$\text{C}_3\text{H}_3\text{O} \Rightarrow \text{C}_2\text{H}_3\text{CO}$	8.510e+14	0.000	14000.00
$\text{C}_3\text{H}_3\text{O} + \text{O}_2 \Rightarrow \text{HCCO} + \text{HCO} + \text{OH}$	5.010e+12	0.000	19192.00
$\text{C}_3\text{H}_4 - \text{P} \rightleftharpoons \text{C}_2\text{H} + \text{CH}_3$	4.200e+16	0.000	100000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O}_2 \Rightarrow \text{HCCO} + \text{OH} + \text{CH}_2$	1.000e+07	1.500	30100.00
$\text{C}_3\text{H}_4 - \text{P} + \text{HO}_2 \Rightarrow \text{C}_2\text{H}_4 + \text{CO} + \text{OH}$	6.090e+09	0.000	7948.00
$\text{C}_3\text{H}_4 - \text{P} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CO} + \text{CH}_2\text{O}$	3.000e+12	0.000	16000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{CHO} + \text{HCO}$	4.500e+12	0.000	16000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{HO}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2\text{O}_2$	5.000e+11	0.000	19000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2\text{O}$	6.500e+02	3.000	200.00
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_3$	2.000e-04	4.500	-1000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} \rightleftharpoons \text{HCO} + \text{C}_2\text{H}_4$	1.000e-04	4.500	-1000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{C}_2\text{H}_3$	1.000e-04	4.500	-1000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{H}$	1.000e-04	4.500	-1000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_2$	6.400e+12	0.000	2100.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \rightleftharpoons \text{C}_2\text{H}_3 + \text{HCO}$	3.200e+12	0.000	2100.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \rightleftharpoons \text{HCCO} + \text{CH}_3$	9.180e+12	0.000	2100.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \rightleftharpoons \text{CH}_2\text{O} + \text{C}_2\text{H}_2$	3.200e+11	0.000	2100.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \Rightarrow \text{HCCO} + \text{CH}_2 + \text{H}$	3.200e+11	0.000	2010.00
$\text{C}_3\text{H}_4 - \text{P} + \text{H} \rightleftharpoons \text{C}_3\text{H}_3 + \text{H}_2$	2.000e+14	0.000	15000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{CH}_3 \rightleftharpoons \text{C}_3\text{H}_3 + \text{CH}_4$	4.000e+11	0.000	7700.00
$\text{C}_3\text{H}_4 - \text{P} + \text{C}_2\text{H}_3 \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_2\text{H}_4$	1.000e+11	0.000	7700.00
$\text{C}_3\text{H}_4 - \text{P} + \text{C}_2\text{H} \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_2\text{H}_2$	4.200e+16	0.000	100000.00
$\text{C}_3\text{H}_4 - \text{P} + \text{O} \rightleftharpoons \text{C}_3\text{H}_3 + \text{OH}$	7.650e+08	1.500	8600.00
<i>Enhanced Collision. Efficiencies: REV = 2.177E+008, 1.31 = 22470</i>			
$\text{C}_3\text{H}_4 - \text{P} + \text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_3\text{H}_6$	1.000e+12	0.000	7700.00
<i>Enhanced Collision. Efficiencies: REV = 4.931E+016, -1.73 = 37950</i>			
$\text{C}_3\text{H}_4 - \text{P} + \text{OH} (+ \text{M}) \Rightarrow \text{C}_3\text{H}_4\text{OH} (+ \text{M})$	2.290e+13	0.000	1808.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
Low pressure limit	7.444e+26	-3.100	1808.00
Troe parameters: a=0.17, T***=180			
T*=50000, T**=12772			
$C_3H_4OH \Rightarrow CH_2CO + CH_3$	3.000e+15	0.000	28000.00
$C_3H_4OH \Rightarrow HCO + C_2H_4$	5.000e+14	0.000	28000.00
$C_3H_4OH \Rightarrow CH_2O + C_2H_3$	1.000e+15	0.000	28000.00
$C_3H_4OH \Rightarrow C_2H_3CHO + H$	5.000e+14	0.000	28000.00
$C_3H_2 + CH_2 \rightleftharpoons iC_4H_3 + H$	3.000e+13	0.000	0.00
$C_3H_5O + O_2 \rightleftharpoons C_2H_3CHO + HO_2$	1.000e+12	0.000	6000.00
$C_3H_5O \rightleftharpoons C_2H_3 + CH_2O$	3.390e+14	0.000	22658.00
$C_3H_5O \rightleftharpoons C_2H_3CHO + H$	1.100e+13	0.000	18451.00
$C_2H_5CHO + CH_3O_2 \rightleftharpoons C_2H_5CO + CH_3O_2H$	1.000e+12	0.000	9500.00
$C_2H_5CHO + C_2H_5 \rightleftharpoons C_2H_5CO + C_2H_6$	1.700e+12	0.000	8440.00
$C_2H_5CHO + C_2H_3 \rightleftharpoons C_2H_5CO + C_2H_4$	1.700e+12	0.000	8440.00
$C_2H_5CO_2 + M \rightleftharpoons C_2H_5 + CO_2 + M$	4.400e+15	0.000	10500.00
$C_2H_3CHO + H \rightleftharpoons H_2 + C_2H_3CO$	4.000e+13	0.000	4200.00
$C_2H_3CHO + OH \rightleftharpoons H_2O + C_2H_3CO$	4.200e+12	0.000	500.00
$C_2H_3CHO + HO_2 \rightleftharpoons H_2O_2 + C_2H_3CO$	1.000e+12	0.000	10000.00
$C_2H_3CHO + CH_3 \rightleftharpoons CH_4 + C_2H_3CO$	2.000e-06	5.600	2500.00
$C_2H_3CHO + C_2H_5 \rightleftharpoons C_2H_3CO + C_2H_6$	5.010e+10	0.000	6280.00
$C_2H_3CHO \rightleftharpoons C_2H_3 + HCO$	2.450e+16	0.000	84128.00
$C_2H_3CHO + O \rightleftharpoons C_2H_3CO + OH$	5.010e+12	0.000	1790.00
$C_2H_3CHO + C_2H_3 \rightleftharpoons C_2H_4 + C_2H_3CO$	1.740e+12	0.000	8440.00
$C_2H_3CHO + C_3H_5 - A \rightleftharpoons C_3H_6 + C_2H_3CO$	1.000e+12	0.000	8000.00
$C_2H_3CO + M \rightleftharpoons C_2H_3 + CO + M$	8.600e+15	0.000	23000.00
<i>Enhanced Collision. Efficiencies: H₂O = 16.25, CO = 1.875, CO₂ = 3.75</i>			
CH ₄ = 16.25, C ₂ H ₆ = 16.25			
$C_2H_3CO + HO_2 \rightleftharpoons C_2H_3 + CO_2 + OH$	2.000e+13	0.000	0.00
$CH_3COCO + O_2 \rightleftharpoons CO_2 + CO_2 + CH_3$	3.000e+10	0.000	2870.00
$CH_3COCO + HO_2 \rightleftharpoons OH + CO_2 + CH_3CO$	2.000e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_3\text{CO} + \text{HCO} \rightleftharpoons \text{CH}_3\text{COCHO}$	1.000e+13	0.000	0.00
$\text{CH}_3\text{COCHO} + \text{H} \rightleftharpoons \text{CH}_3\text{COCO} + \text{H}_2$	4.000e+13	0.000	4200.00
$\text{CH}_3\text{COCHO} + \text{OH} \rightleftharpoons \text{CH}_3\text{COCO} + \text{H}_2\text{O}$	2.690e+10	0.760	-340.00
$\text{CH}_3\text{COCHO} + \text{O} \rightleftharpoons \text{CH}_3\text{COCO} + \text{OH}$	5.000e+12	0.000	1790.00
$\text{CH}_3\text{COCHO} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{COCO} + \text{CH}_4$	1.700e+12	0.000	8440.00
$\text{CH}_3\text{COCHO} + \text{HO}_2 \rightleftharpoons \text{CH}_3\text{COCO} + \text{H}_2\text{O}_2$	2.800e+12	0.000	13600.00
$\text{CH}_3\text{CO} + \text{CO} \rightleftharpoons \text{CH}_3\text{COCO}$	1.500e+11	0.000	3000.00
$\text{NC}_4\text{H}_{10} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{H}$	1.580e+16	0.000	97970.00
$\text{NC}_4\text{H}_{10} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{H}$	1.000e+16	0.000	94990.00
$\text{NC}_4\text{H}_{10} \rightleftharpoons \text{NC}_3\text{H}_7 + \text{CH}_3$	1.000e+17	0.000	84650.00
$\text{NC}_4\text{H}_{10} \rightleftharpoons \text{C}_2\text{H}_5 + \text{C}_2\text{H}_5$	1.580e+17	0.000	87040.00
$\text{NC}_4\text{H}_{10} + \text{O}_2 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{HO}_2$	3.970e+13	0.000	50870.00
$\text{NC}_4\text{H}_{10} + \text{O}_2 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{HO}_2$	7.940e+13	0.000	47690.00
$\text{NC}_4\text{H}_{10} + \text{H} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{H}_2$	1.880e+05	2.750	6280.00
$\text{NC}_4\text{H}_{10} + \text{H} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{H}_2$	2.600e+06	2.400	4471.00
$\text{NC}_4\text{H}_{10} + \text{O} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{OH}$	1.930e+05	2.680	3716.00
$\text{NC}_4\text{H}_{10} + \text{O} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{OH}$	9.540e+04	2.710	2106.00
$\text{NC}_4\text{H}_{10} + \text{OH} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{H}_2\text{O}$	1.050e+10	0.970	1590.00
$\text{NC}_4\text{H}_{10} + \text{OH} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{H}_2\text{O}$	9.360e+07	1.610	-35.00
$\text{NC}_4\text{H}_{10} + \text{HO}_2 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{H}_2\text{O}_2$	1.680e+13	0.000	20440.00
$\text{NC}_4\text{H}_{10} + \text{HO}_2 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{H}_2\text{O}_2$	1.120e+13	0.000	17690.00
$\text{NC}_4\text{H}_{10} + \text{HCO} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CH}_2\text{O}$	2.040e+05	2.500	18500.00
$\text{NC}_4\text{H}_{10} + \text{HCO} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{CH}_2\text{O}$	2.160e+07	1.900	17000.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CH}_4$	9.040e-01	3.650	7154.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{CH}_4$	5.410e+04	2.260	7287.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3\text{O} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CH}_3\text{OH}$	3.162e+11	0.000	7000.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3\text{O} \rightleftharpoons \text{sC}_4\text{H}_9 + \text{CH}_3\text{OH}$	2.190e+11	0.000	5000.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CH}_3\text{O}_2\text{H}$	1.680e+13	0.000	20440.00
$\text{NC}_4\text{H}_{10} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{CH}_3\text{O}_2\text{H}$	1.120e+13	0.000	17690.00
$\text{NC}_4\text{H}_{10} + \text{C}_2\text{H}_3 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{C}_2\text{H}_4$	1.020e+12	0.000	18000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{NC}_4\text{H}_{10} + \text{C}_2\text{H}_3 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{C}_2\text{H}_4$	8.000e+11	0.000	16800.00
$\text{NC}_4\text{H}_{10} + \text{C}_2\text{H}_5 \rightleftharpoons \text{PC}_4\text{H}_9 + \text{C}_2\text{H}_6$	1.020e+11	0.000	13400.00
$\text{NC}_4\text{H}_{10} + \text{C}_2\text{H}_5 \rightleftharpoons \text{sC}_4\text{H}_9 + \text{C}_2\text{H}_6$	1.000e+11	0.000	10400.00
$\text{PC}_4\text{H}_9 \rightleftharpoons \text{sC}_4\text{H}_9$	3.800e+10	0.670	36600.00
$\text{PC}_4\text{H}_9 \rightleftharpoons \text{C}_2\text{H}_5 + \text{C}_2\text{H}_4$	6.460e+25	-11.900	32200.00
$\text{PC}_4\text{H}_9 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}$	1.260e+13	0.000	38600.00
$\text{PC}_4\text{H}_9 + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2\text{O}_2$	2.410e+13	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2\text{O}$	2.400e+13	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{H} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2$	1.250e+13	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{CH}_4$	2.000e+12	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{C}_2\text{H}_6$	1.600e+12	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{C}_3\text{H}_5 - \text{A} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{C}_3\text{H}_6$	1.000e+12	0.000	0.00
$\text{PC}_4\text{H}_9 + \text{C}_4\text{H}_7 - 3 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{C}_4\text{H}_8 - 1$	1.000e+12	0.000	0.00
$\text{sC}_4\text{H}_9 + \text{M} \rightleftharpoons \text{C}_3\text{H}_6 + \text{CH}_3 + \text{M}$	2.000e+13	0.000	31000.00
$\text{PC}_4\text{H}_9 + \text{M} \rightleftharpoons \text{C}_3\text{H}_6 + \text{CH}_3 + \text{M}$	2.000e+13	0.000	31000.00
$\text{sC}_4\text{H}_9 + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2\text{O}_2$	2.400e+13	0.000	0.00
$\text{sC}_4\text{H}_9 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2\text{O}$	2.400e+13	0.000	0.00
$\text{sC}_4\text{H}_9 + \text{H} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{H}_2$	3.333e+13	0.000	0.00
$\text{sC}_4\text{H}_9 + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{CH}_4$	8.000e+11	0.000	0.00
$\text{C}_4\text{H}_8 - 1 \rightleftharpoons \text{C}_4\text{H}_7 - 3 + \text{H}$	4.078e+18	-1.000	97350.00
$\text{C}_3\text{H}_5 - \text{A} + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_8 - 1$	1.020e+14	-0.320	-130.00
$\text{C}_4\text{H}_8 - 1 + \text{O}_2 \rightleftharpoons \text{C}_4\text{H}_7 - 3 + \text{HO}_2$	4.000e+12	0.000	40000.00
$\text{C}_4\text{H}_8 - 1 + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_7 - 3 + \text{H}_2\text{O}_2$	1.000e+11	0.000	17060.00
$\text{C}_4\text{H}_8 - 1 + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_7 - 4 + \text{H}_2\text{O}_2$	6.000e+11	0.000	17000.00
$\text{C}_4\text{H}_8 - 1 + \text{HO}_2 \Rightarrow \text{CH}_2\text{O} + \text{C}_3\text{H}_6 + \text{OH}$	2.500e+12	0.000	14340.00
$\text{C}_4\text{H}_8 - 1 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_7 - 3 + \text{H}_2\text{O}$	4.186e+06	2.000	-543.00
$\text{C}_4\text{H}_8 - 1 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_7 - 4 + \text{H}_2\text{O}$	2.670e+06	2.000	450.00
$\text{C}_4\text{H}_8 - 1 + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{NC}_3\text{H}_7$	2.000e+12	0.000	-928.00
$\text{C}_4\text{H}_8 - 1 + \text{OH} \rightleftharpoons \text{CH}_3 + \text{C}_2\text{H}_5\text{CHO}$	6.800e+11	0.000	-928.00
$\text{C}_4\text{H}_8 - 1 + \text{O} \rightleftharpoons \text{C}_3\text{H}_6 + \text{CH}_2\text{O}$	7.230e+05	2.340	-1050.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_4H_8 - 1 + O \rightleftharpoons CH_3CHO + C_2H_4$	1.300e+13	0.000	850.00
$C_4H_8 - 1 + O \rightleftharpoons C_2H_5 + CH_3CO$	1.625e+13	0.000	850.00
$C_4H_8 - 1 + O \rightleftharpoons C_4H_7 - 3 + OH$	2.600e+12	0.000	4500.00
$C_4H_8 - 1 + O \rightleftharpoons C_4H_7 - 4 + OH$	5.100e+13	0.000	7850.00
$C_4H_8 - 1 + H \rightleftharpoons C_4H_7 - 3 + H_2$	1.950e+13	0.000	4445.00
$C_4H_8 - 1 + H \rightleftharpoons C_4H_7 - 4 + H_2$	2.850e+07	2.000	7700.00
$C_4H_8 - 1 + CH_3 \rightleftharpoons C_4H_7 - 4 + CH_4$	3.000e-01	4.000	8200.00
$C_4H_8 - 1 + CH_3 \rightleftharpoons C_4H_7 - 3 + CH_4$	1.000e+11	0.000	7300.00
$C_4H_8 - 1 + C_2H_5 \rightleftharpoons C_4H_7 - 3 + C_2H_6$	1.000e+11	0.000	8300.00
$C_4H_8 - 1 + C_2H_3 \rightleftharpoons C_4H_7 - 3 + C_2H_4$	7.200e+11	0.000	5008.00
$C_4H_8 - 1 + C_3H_5 - A \rightleftharpoons C_4H_7 - 3 + C_3H_6$	8.000e+10	0.000	12400.00
$C_4H_8 - 1 + C_3H_5 - s \rightleftharpoons C_4H_7 - 3 + C_3H_6$	8.000e+10	0.000	12400.00
$C_4H_8 - 1 + C_3H_5 - t \rightleftharpoons C_4H_7 - 3 + C_3H_6$	8.000e+10	0.000	12400.00
$C_4H_8 - 1 + H \rightleftharpoons C_3H_6 + CH_3$	7.230e+12	0.000	1302.00
$C_4H_7 - 4 \rightleftharpoons C_2H_4 + C_2H_3$	5.000e+13	0.000	38000.00
$C_4H_7 - 4 \rightleftharpoons C_4H_6 + H$	3.160e+13	0.000	34780.00
$C_4H_7 - 4 + O_2 \rightleftharpoons C_4H_6 + HO_2$	1.020e+12	0.000	22654.00
$C_4H_7 - 4 + HO_2 \rightleftharpoons C_4H_6 + H_2O_2$	1.800e+12	0.000	0.00
$C_4H_7 - 4 + HO_2 \rightleftharpoons C_3H_5 - A + CH_2O + OH$	1.000e+12	0.000	0.00
$C_4H_7 - 4 + OH \rightleftharpoons C_4H_6 + H_2O$	4.000e+13	0.000	0.00
$C_4H_7 - 4 + O \rightleftharpoons C_4H_6 + OH$	4.000e+13	0.000	0.00
$C_4H_7 - 4 + H \rightleftharpoons C_4H_6 + H_2$	3.160e+13	0.000	0.00
$C_4H_7 - 4 + CH_3 \rightleftharpoons C_4H_6 + CH_4$	7.940e+12	0.000	0.00
$C_4H_7 - 4 + C_2H_3 \rightleftharpoons C_4H_6 + C_2H_4$	4.000e+12	0.000	0.00
$C_4H_7 - 4 + C_2H_5 \rightleftharpoons C_4H_6 + C_2H_6$	4.000e+12	0.000	0.00
$C_4H_7 - 4 + C_2H_5 \rightleftharpoons C_4H_8 - 1 + C_2H_4$	5.000e+11	0.000	0.00
$C_4H_7 - 4 + C_3H_3 \rightleftharpoons C_4H_6 + C_3H_4 - P$	4.000e+12	0.000	0.00
$C_4H_7 - 4 + C_3H_3 \rightleftharpoons C_4H_6 + C_3H_4 - A$	4.000e+12	0.000	0.00
$C_4H_7 - 4 + C_3H_5 - A \rightleftharpoons C_4H_6 + C_3H_6$	6.300e+12	0.000	0.00
$C_4H_7 - 4 + C_4H_7 - 4 \rightleftharpoons C_4H_6 + C_4H_8 - 1$	3.160e+12	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_4H_7 - 4 + C_2H_6 \rightleftharpoons C_4H_8 - 1 + C_2H_5$	3.000e+13	0.000	12300.00
$C_4H_7 - 4 + C_2H_4 \rightleftharpoons C_4H_8 - 1 + C_2H_3$	1.000e+11	0.000	15000.00
$C_4H_7 - 4 + C_3H_6 \rightleftharpoons C_4H_8 - 1 + C_3H_5 - A$	1.000e+11	0.000	9800.00
$C_4H_7 - 4 + C_4H_8 - 1 \rightleftharpoons C_4H_8 - 1 + C_4H_7 - 3$	1.000e+11	0.000	8300.00
$C_4H_6 + C_4H_7 - 4 \rightleftharpoons NC_4H_5 + C_4H_8 - 1$	6.320e+02	3.130	20010.00
$C_4H_6 + C_4H_7 - 4 \rightleftharpoons iC_4H_5 + C_4H_8 - 1$	6.320e+02	3.130	18010.00
$C_4H_7 - 3 \rightleftharpoons C_4H_6 + H$	1.200e+14	0.000	49300.00
$C_4H_7 - 3 + O_2 \rightleftharpoons C_4H_6 + HO_2$	2.000e+09	0.000	-1506.00
$C_4H_7 - 3 + HO_2 \rightleftharpoons C_4H_6 + H_2O_2$	1.000e+12	0.000	0.00
$C_4H_7 - 3 + HO_2 \Rightarrow C_2H_3CHO + CH_3 + OH$	7.000e+12	0.000	-1000.00
$C_4H_7 - 3 + OH \rightleftharpoons C_4H_6 + H_2O$	4.000e+13	0.000	0.00
$C_4H_7 - 3 + O \rightleftharpoons C_4H_6 + OH$	4.000e+13	0.000	0.00
$C_4H_7 - 3 + O \rightleftharpoons C_2H_3CHO + CH_3$	6.030e+13	0.000	0.00
$C_4H_7 - 3 + H \rightleftharpoons C_4H_6 + H_2$	3.160e+12	0.000	0.00
$C_4H_7 - 3 + CH_3 \rightleftharpoons C_4H_6 + CH_4$	1.000e+13	0.000	0.00
$C_4H_7 - 3 + C_2H_3 \rightleftharpoons C_4H_6 + C_2H_4$	4.000e+12	0.000	0.00
$C_4H_7 - 3 + C_2H_5 \rightleftharpoons C_4H_6 + C_2H_6$	4.000e+12	0.000	0.00
$C_4H_7 - 3 + C_2H_5 \rightleftharpoons C_4H_8 - 1 + C_2H_4$	5.000e+11	0.000	0.00
$C_4H_7 - 3 + C_3H_3 \rightleftharpoons C_4H_6 + C_3H_4 - P$	4.000e+12	0.000	0.00
$C_4H_7 - 3 + C_3H_3 \rightleftharpoons C_4H_6 + C_3H_4 - A$	4.000e+12	0.000	0.00
$C_4H_7 - 3 + C_3H_5 - A \rightleftharpoons C_4H_6 + C_3H_6$	6.300e+12	0.000	0.00
$C_4H_7 - 3 + C_3H_5 - A \rightleftharpoons C_4H_8 - 1 + C_3H_4 - A$	1.000e+12	0.000	0.00
$C_4H_7 - 3 + C_4H_7 - 3 \rightleftharpoons C_4H_6 + C_4H_8 - 1$	3.000e+12	0.000	0.00
$C_4H_7 - 1 \rightleftharpoons C_2H_2 + C_2H_5$	2.000e+13	0.000	33000.00
$C_4H_7 - 1 \rightleftharpoons C_4H_7 - 4$	1.500e+08	1.000	29400.00
$C_4H_7 - 1 \rightleftharpoons C_4H_7 - 3$	1.670e+13	1.000	34500.00
$C_4H_7 - 1 + O_2 \rightleftharpoons HCO + C_2H_5CHO$	4.600e+16	-1.390	1010.00
$C_4H_7 - 1 + CH_2O \rightleftharpoons C_4H_8 - 1 + HCO$	5.420e+03	2.810	5862.00
$C_4H_6 \rightleftharpoons C_2H_4 + C_2H_2$	1.000e+14	0.000	75000.00
$C_4H_6 \rightleftharpoons NC_4H_5 + H$	1.580e+16	0.000	110000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_4H_6 + O_2 \rightleftharpoons NC_4H_5 + HO_2$	2.800e+13	0.000	62500.00
$C_4H_6 + O_2 \rightleftharpoons iC_4H_5 + HO_2$	1.400e+12	0.000	50600.00
$C_4H_6 + HO_2 \rightleftharpoons NC_4H_5 + H_2O_2$	4.000e+11	0.000	12600.00
$C_4H_6 + HO_2 \rightleftharpoons iC_4H_5 + H_2O_2$	2.000e+11	0.000	9920.00
$C_4H_6 + OH \rightleftharpoons NC_4H_5 + H_2O$	1.000e+07	2.000	7253.00
$C_4H_6 + OH \rightleftharpoons iC_4H_5 + H_2O$	8.000e+06	2.000	3744.00
$C_4H_6 + O \rightleftharpoons NC_4H_5 + OH$	4.530e+15	-0.475	7028.00
$C_4H_6 + O \rightleftharpoons iC_4H_5 + OH$	2.270e+15	-0.475	7028.00
$C_4H_6 + H \rightleftharpoons C_3H_4 - P + CH_3$	1.300e+04	2.500	1000.00
$C_4H_6 + H \rightleftharpoons C_3H_4 - A + CH_3$	1.000e+13	0.000	15000.00
$C_4H_6 + H \rightleftharpoons NC_4H_5 + H_2$	5.000e+15	0.000	22800.00
$C_4H_6 + H \rightleftharpoons iC_4H_5 + H_2$	2.500e+15	0.000	22800.00
$C_4H_6 + CH_3 \rightleftharpoons NC_4H_5 + CH_4$	4.000e+14	0.000	22800.00
$C_4H_6 + CH_3 \rightleftharpoons iC_4H_5 + CH_4$	2.000e+14	0.000	22800.00
$C_4H_6 + C_2H_3 \rightleftharpoons NC_4H_5 + C_2H_4$	6.320e+02	3.130	20010.00
$C_4H_6 + C_2H_3 \rightleftharpoons iC_4H_5 + C_2H_4$	6.320e+02	3.130	18010.00
$C_2H_3CHO + C_2H_3 \rightleftharpoons C_4H_6 + HCO$	2.800e+21	-2.440	14720.00
$C_4H_6 \rightleftharpoons C_4H_4 + H_2$	2.500e+15	0.000	94700.00
$C_4H_6 + HO_2 \rightleftharpoons C_4H_6O_{25} + OH$	1.200e+12	0.000	14000.00
$C_4H_6 + HO_2 \rightleftharpoons C_2H_3CHOCH_2 + OH$	4.800e+12	0.000	14000.00
$C_2H_3CHOCH_2 \rightleftharpoons C_4H_6O_{23}$	2.000e+14	0.000	50600.00
$C_4H_6O_{23} \rightleftharpoons C_2H_4 + CH_2CO$	5.750e+15	0.000	69300.00
$C_4H_6O_{23} \rightleftharpoons C_2H_2 + C_2H_4O_{12}$	1.000e+16	0.000	75800.00
$C_4H_6O_{25} \rightleftharpoons C_4H_4O + H_2$	5.300e+12	0.000	48500.00
$C_4H_4O \rightleftharpoons CO + C_3H_4 - P$	1.780e+15	0.000	77500.00
$C_4H_4O \rightleftharpoons C_2H_2 + CH_2CO$	5.010e+14	0.000	77500.00
$C_4H_6 + OH \rightleftharpoons HOC_4H_6$	7.000e+12	0.000	-994.00
$HOC_4H_6 \Rightarrow OC_4H_6 + H$	5.000e+15	0.000	28000.00
$C_4H_6 + O \Rightarrow OC_4H_6$	3.000e+13	0.000	80.00
$OC_4H_6 \Rightarrow C_3H_6 + CO$	2.000e+13	0.000	57000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{OC}_4\text{H}_6 \Rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{CO}$	5.000e+14	1.000	78000.00
$\text{OC}_4\text{H}_6 + \text{O} \Rightarrow \text{CH}_2\text{CHO} + \text{CH}_2\text{CHO}$	1.200e+08	1.440	530.00
$\text{OC}_4\text{H}_6 + \text{OH} \Rightarrow \text{CH}_2\text{CO} + \text{C}_2\text{H}_3 + \text{H}_2\text{O}$	2.024e+13	0.000	5955.00
$\text{OC}_4\text{H}_6 + \text{HO}_2 \Rightarrow \text{CH}_2\text{CHO} + \text{CH}_2\text{CHO} + \text{OH}$	5.000e+12	0.000	14964.00
$\text{OC}_4\text{H}_6 + \text{H} \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{H}_2$	4.100e+09	1.160	2405.00
$\text{OC}_4\text{H}_6 + \text{OH} \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{H}_2\text{O}$	2.350e+10	0.730	-1113.00
$\text{OC}_4\text{H}_6 + \text{HO}_2 \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{H}_2\text{O}_2$	1.700e+12	0.000	10700.00
$\text{OC}_4\text{H}_6 + \text{O} \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{OH}$	5.850e+12	0.000	1808.00
$\text{OC}_4\text{H}_6 + \text{CH}_3 \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{CH}_4$	1.700e+12	0.000	8440.00
$\text{OC}_4\text{H}_6 + \text{C}_2\text{H}_3 \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{C}_2\text{H}_4$	1.700e+12	0.000	8440.00
$\text{OC}_4\text{H}_6 + \text{C}_3\text{H}_5 - \text{A} \Rightarrow \text{C}_4\text{H}_5\text{O} + \text{C}_3\text{H}_6$	1.700e+12	0.000	8440.00
$\text{C}_4\text{H}_5\text{O} + \text{O}_2 \Rightarrow \text{C}_2\text{H}_3\text{CHO} + \text{CO} + \text{OH}$	1.000e+12	0.000	25000.00
$\text{C}_4\text{H}_5\text{O} \Rightarrow \text{CH}_2\text{CO} + \text{C}_2\text{H}_3$	1.000e+15	0.000	65000.00
$\text{C}_4\text{H}_5\text{O} \Rightarrow \text{CO} + \text{C}_2\text{H}_2 + \text{CH}_3$	1.000e+15	0.000	65000.00
$\text{C}_4\text{H}_5\text{O} \Rightarrow \text{CO} + \text{C}_3\text{H}_5 - \text{A}$	5.000e+14	0.000	60000.00
$\text{iC}_4\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{CO} + \text{CH}_2\text{O}$	2.000e+11	0.000	14000.00
$\text{iC}_4\text{H}_5 + \text{O} \Rightarrow \text{CH}_2\text{CO} + \text{C}_2\text{H}_3$	1.000e+13	0.000	2000.00
$\text{iC}_4\text{H}_5 + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{C}_2\text{H}_3 + \text{OH}$	1.000e+12	0.000	2000.00
$\text{C}_3\text{H}_6 + \text{iC}_4\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_5 - \text{A} + \text{C}_4\text{H}_6$	1.000e+11	0.000	9800.00
$\text{iC}_4\text{H}_5 + \text{CH}_2\text{O} \rightleftharpoons \text{C}_4\text{H}_6 + \text{HCO}$	4.000e+12	0.000	8840.00
$\text{C}_2\text{H}_3 + \text{C}_2\text{H}_2 (+ \text{M}) \rightleftharpoons \text{iC}_4\text{H}_5 (+ \text{M})$	1.000e+04	2.350	17900.00
Low pressure limit	2.600e+38	-7.410	7500.00
$\text{iC}_4\text{H}_5 (+ \text{M}) \rightleftharpoons \text{C}_4\text{H}_4 + \text{H} (+ \text{M})$	1.000e+14	0.000	50000.00
Low pressure limit	2.000e+15	0.000	42000.00
$\text{NC}_4\text{H}_5 (+ \text{M}) \rightleftharpoons \text{C}_4\text{H}_4 + \text{H} (+ \text{M})$	1.000e+14	0.000	37000.00
Low pressure limit	1.000e+14	0.000	30000.00
$\text{NC}_4\text{H}_5 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{HCO}$	2.000e+11	0.000	14000.00
$\text{NC}_4\text{H}_5 + \text{O} \Rightarrow \text{C}_3\text{H}_5 - \text{A} + \text{CO}$	1.000e+13	0.000	2000.00
$\text{NC}_4\text{H}_5 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}_2\text{O}$	2.000e+07	2.000	1000.00
$\text{NC}_4\text{H}_5 + \text{HO}_2 \Rightarrow \text{C}_3\text{H}_5 - \text{A} + \text{CO} + \text{OH}$	1.000e+13	0.000	0.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{NC}_4\text{H}_5 + \text{H} \rightleftharpoons \text{C}_4\text{H}_4 + \text{H}_2$	1.000e+14	0.000	0.00
$\text{NC}_4\text{H}_5 + \text{CH}_2\text{O} \rightleftharpoons \text{C}_4\text{H}_6 + \text{HCO}$	4.000e+12	0.000	8840.00
$\text{C}_3\text{H}_6 + \text{NC}_4\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_5 + \text{A} + \text{C}_4\text{H}_6$	1.000e+11	0.000	9800.00
$\text{C}_4\text{H}_4 \rightleftharpoons \text{C}_2\text{H}_2 + \text{C}_2\text{H}_2$	3.200e+13	0.000	77100.00
$\text{C}_4\text{H}_4 + \text{M} \rightleftharpoons \text{NC}_4\text{H}_3 + \text{H} + \text{M}$	1.000e+20	0.000	99300.00
$\text{C}_4\text{H}_4 \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}_2$	1.260e+15	0.000	94700.00
$\text{C}_4\text{H}_4 + \text{O}_2 \rightleftharpoons \text{NC}_4\text{H}_3 + \text{HO}_2$	1.000e+13	0.000	63200.00
$\text{C}_4\text{H}_4 + \text{O}_2 \rightleftharpoons \text{iC}_4\text{H}_3 + \text{HO}_2$	1.000e+13	0.000	44640.00
$\text{C}_4\text{H}_4 + \text{HO}_2 \rightleftharpoons \text{NC}_4\text{H}_3 + \text{H}_2\text{O}_2$	2.000e+11	0.000	12600.00
$\text{C}_4\text{H}_4 + \text{HO}_2 \rightleftharpoons \text{iC}_4\text{H}_3 + \text{H}_2\text{O}_2$	1.000e+11	0.000	9920.00
$\text{C}_4\text{H}_4 + \text{HO}_2 \rightleftharpoons \text{C}_3\text{H}_3 + \text{HCO} + \text{OH}$	4.000e+11	0.000	8000.00
$\text{C}_4\text{H}_4 + \text{O} \rightleftharpoons \text{C}_3\text{H}_4 + \text{A} + \text{CO}$	3.000e+13	0.000	1810.00
$\text{C}_4\text{H}_4 + \text{H} \rightleftharpoons \text{NC}_4\text{H}_3 + \text{H}_2$	6.650e+05	2.530	12240.00
$\text{C}_4\text{H}_4 + \text{H} \rightleftharpoons \text{iC}_4\text{H}_3 + \text{H}_2$	3.330e+05	2.530	9240.00
$\text{C}_4\text{H}_4 + \text{OH} \rightleftharpoons \text{NC}_4\text{H}_3 + \text{H}_2\text{O}$	3.100e+07	2.000	3430.00
$\text{C}_4\text{H}_4 + \text{OH} \rightleftharpoons \text{iC}_4\text{H}_3 + \text{H}_2\text{O}$	1.550e+07	2.000	430.00
$\text{C}_4\text{H}_4 + \text{O} \rightleftharpoons \text{C}_3\text{H}_3 + \text{HCO}$	6.000e+08	1.450	-860.00
$\text{iC}_4\text{H}_3 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CO} + \text{HCCO}$	1.000e+12	0.000	0.00
$\text{iC}_4\text{H}_3 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}_2\text{O}$	3.000e+13	0.000	0.00
$\text{iC}_4\text{H}_3 + \text{O} \rightleftharpoons \text{H}_2\text{C}_4\text{O} + \text{H}$	2.000e+13	0.000	0.00
$\text{iC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}_2$	5.000e+13	0.000	0.00
$\text{iC}_4\text{H}_3(+ \text{M}) \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}(+ \text{M})$	1.000e+14	0.000	55000.00
Low pressure limit	2.500e+15	0.000	48000.00
$\text{NC}_4\text{H}_3(+ \text{M}) \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}(+ \text{M})$	1.000e+14	0.000	36000.00
Low pressure limit	1.000e+14	0.000	30000.00
$\text{NC}_4\text{H}_3 + \text{OH} \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}_2\text{O}$	3.000e+13	0.000	0.00
$\text{NC}_4\text{H}_3 + \text{H} \rightleftharpoons \text{C}_4\text{H}_2 + \text{H}_2$	5.000e+13	0.000	0.00
$\text{C}_2\text{H}_2 + \text{C}_2\text{H}(+ \text{M}) \rightleftharpoons \text{NC}_4\text{H}_3(+ \text{M})$	8.300e+10	0.899	-363.00
Low pressure limit	1.240e+31	-4.718	1871.00
Troe parameters: a=1, T***=100			

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
T*=5613, T**=13387			
<i>Enhanced Collision. Efficiencies: H₂ = 2, H₂O = 6, CH₄ = 2, CO = 1.5</i>			
CO ₂ = 2, C ₂ H ₆ = 3, C ₂ H ₂ = 2.5, C ₂ H ₄ = 2.5			
C ₂ H ₂ + C ₂ H(+ M)⇌iC ₄ H ₃ (+ M)	8.300e+10	0.899	-363.00
Low pressure limit	1.240e+31	-4.718	1871.00
Troe parameters: a=1, T***=100			
T*=5613, T**=13387			
<i>Enhanced Collision. Efficiencies: H₂ = 2, H₂O = 6, CH₄ = 2, CO = 1.5</i>			
CO ₂ = 2, C ₂ H ₆ = 3, C ₂ H ₂ = 2.5, C ₂ H ₄ = 2.5			
H ₂ C ₄ O + OH⇌CH ₂ CO + HCCO	1.000e+07	2.000	2000.00
H ₂ C ₄ O + H⇌C ₂ H ₂ + HCCO	5.000e+13	0.000	3000.00
C ₄ H ₂ + OH⇌H ₂ C ₄ O + H	6.660e+12	0.000	-410.00
C ₄ H ₂ + O⇌C ₃ H ₂ + CO	1.200e+12	0.000	0.00
sC ₄ H ₉ OH + H⇌sC ₄ H ₉ O + H ₂	5.360e+04	2.530	4405.00
sC ₄ H ₉ OH + OH⇌sC ₄ H ₉ O + H ₂ O	1.500e+10	0.800	2534.00
sC ₄ H ₉ OH + O⇌sC ₄ H ₉ O + OH	1.460e-03	4.730	1727.00
sC ₄ H ₉ OH + HO ₂ ⇌sC ₄ H ₉ O + H ₂ O ₂	2.500e+12	0.000	24000.00
sC ₄ H ₉ OH + CH ₃ ⇌sC ₄ H ₉ O + CH ₄	1.020e+00	3.570	8221.00
sC ₄ H ₉ OH + HCO⇌sC ₄ H ₉ O + CH ₂ O	3.400e+04	2.500	13500.00
sC ₄ H ₉ OH + CH ₃ O⇌sC ₄ H ₉ O + CH ₃ OH	2.300e+10	0.000	2900.00
sC ₄ H ₉ OH + CH ₃ O ₂ ⇌sC ₄ H ₉ O + CH ₃ O ₂ H	1.500e+12	0.000	15000.00
sC ₄ H ₉ OH + C ₂ H ₅ ⇌sC ₄ H ₉ O + C ₂ H ₆	1.000e+11	0.000	9200.00
sC ₄ H ₉ OH + PC ₄ H ₉ ⇌sC ₄ H ₉ O + NC ₄ H ₁₀	1.000e+11	0.000	9200.00
sC ₄ H ₉ OH + sC ₄ H ₉ ⇌sC ₄ H ₉ O + NC ₄ H ₁₀	1.000e+11	0.000	9200.00
iC ₃ H ₇ CHO⇌iC ₃ H ₇ CO + H	5.000e+15	0.000	85000.00
iC ₃ H ₇ CHO⇌iC ₃ H ₇ + HCO	1.129e+17	-0.030	79760.00
iC ₃ H ₇ CHO⇌CH ₃ CHCHO + CH ₃	2.000e+17	0.000	84650.00
iC ₃ H ₇ CHO + O ₂ ⇌iC ₃ H ₇ CO + HO ₂	4.000e+13	0.000	37600.00
iC ₃ H ₇ CHO + H⇌iC ₃ H ₇ CO + H ₂	2.600e+12	0.000	2600.00
iC ₃ H ₇ CHO + O⇌iC ₃ H ₇ CO + OH	7.180e+12	0.000	1389.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$iC_3H_7CHO + OH \rightleftharpoons iC_3H_7CO + H_2O$	2.406e+12	0.000	-781.00
$iC_3H_7CHO + HO_2 \rightleftharpoons iC_3H_7CO + H_2O_2$	3.000e+12	0.000	11920.00
$iC_3H_7CHO + CH_3 \rightleftharpoons iC_3H_7CO + CH_4$	3.980e+12	0.000	8700.00
$iC_3H_7CHO + HCO \rightleftharpoons iC_3H_7CO + CH_2O$	3.980e+12	0.000	8700.00
$iC_3H_7CHO + CH_3O \rightleftharpoons iC_3H_7CO + CH_3OH$	1.150e+11	0.000	1280.00
$iC_3H_7CHO + CH_3O_2 \rightleftharpoons iC_3H_7CO + CH_3O_2H$	1.000e+12	0.000	9500.00
$iC_3H_7CHO + C_2H_5 \rightleftharpoons iC_3H_7CO + C_2H_6$	1.700e+12	0.000	8440.00
$iC_3H_7CHO + C_2H_3 \rightleftharpoons iC_3H_7CO + C_2H_4$	1.700e+12	0.000	8440.00
$iC_3H_7CO \rightleftharpoons iC_3H_7 + CO$	1.426e+13	-0.040	10950.00
$iC_3H_5CO \rightleftharpoons C_3H_5 - t + CO$	4.780e+12	0.000	27470.00
$NC_3H_7CHO \Rightarrow NC_3H_7 + HCO$	6.000e+14	0.000	79100.00
$NC_3H_7CHO \rightleftharpoons C_2H_5 + CH_2CHO$	1.580e+17	0.000	80280.00
$PC_4H_9 + O_2 \rightleftharpoons C_4H_{91}O_2$	9.000e+18	-2.500	0.00
$sC_4H_9 + O_2 \rightleftharpoons C_4H_{92}O_2$	1.700e+19	-2.500	0.00
$C_4H_{91}O_2 \rightleftharpoons C_4H_8 - 1 + HO_2$	5.044e+38	-8.110	41490.00
$C_4H_{92}O_2 \rightleftharpoons C_4H_8 - 1 + HO_2$	5.075e+42	-9.410	42490.00
$C_4H_{91}O_2 + HO_2 \rightleftharpoons C_4H_{91}O_2H + O_2$	2.113e+10	0.000	-3640.00
$C_4H_{91}O_2 + H_2O_2 \rightleftharpoons C_4H_{91}O_2H + HO_2$	2.410e+12	0.000	9936.00
$C_4H_{91}O_2 + HO_2 \Rightarrow PC_4H_9O + OH + O_2$	1.400e+16	-1.610	1860.00
$C_4H_{91}O_2 + CH_3O_2 \Rightarrow PC_4H_9O + CH_3O + O_2$	1.400e+16	-1.610	1860.00
$C_4H_{91}O_2 + C_4H_{91}O_2 \Rightarrow PC_4H_9O + PC_4H_9O + O_2$	1.400e+16	-1.610	1860.00
$C_4H_{91}O_2H \rightleftharpoons PC_4H_9O + OH$	1.500e+16	0.000	42500.00
$PC_4H_9O \rightleftharpoons CH_2O + NC_3H_7$	2.000e+13	0.000	20000.00
$PC_4H_9O + O_2 \rightleftharpoons NC_3H_7CHO + HO_2$	8.430e+09	0.000	220.00
$C_4H_{92}O_2 + HO_2 \rightleftharpoons C_4H_{92}O_2H + O_2$	2.113e+10	0.000	-3640.00
$C_4H_{92}O_2 + H_2O_2 \rightleftharpoons C_4H_{92}O_2H + HO_2$	2.410e+12	0.000	9936.00
$C_4H_{92}O_2H \rightleftharpoons sC_4H_9O + OH$	9.450e+15	0.000	41600.00
$sC_4H_9O \rightleftharpoons CH_3CHO + C_2H_5$	2.000e+13	0.000	20000.00
$sC_4H_9O \rightleftharpoons CH_3 + C_2H_5CHO$	2.000e+13	0.000	20000.00
$C_4H_{91}O_2 + PC_4H_9 \rightleftharpoons PC_4H_9O + PC_4H_9O$	7.000e+12	0.000	-1000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_4\text{H}_{91}\text{O}_2 + \text{sC}_4\text{H}_9 \rightleftharpoons \text{PC}_4\text{H}_9\text{O} + \text{sC}_4\text{H}_9\text{O}$	7.000e+12	0.000	-1000.00
$\text{C}_4\text{H}_{92}\text{O}_2 + \text{PC}_4\text{H}_9 \rightleftharpoons \text{sC}_4\text{H}_9\text{O} + \text{PC}_4\text{H}_9\text{O}$	7.000e+12	0.000	-1000.00
$\text{C}_4\text{H}_{92}\text{O}_2 + \text{sC}_4\text{H}_9 \rightleftharpoons \text{sC}_4\text{H}_9\text{O} + \text{sC}_4\text{H}_9\text{O}$	7.000e+12	0.000	-1000.00
$\text{PC}_4\text{H}_9 + \text{HO}_2 \rightleftharpoons \text{PC}_4\text{H}_9\text{O} + \text{OH}$	7.000e+12	0.000	-1000.00
$\text{sC}_4\text{H}_9 + \text{HO}_2 \rightleftharpoons \text{sC}_4\text{H}_9\text{O} + \text{OH}$	7.000e+12	0.000	-1000.00
$\text{C}_4\text{H}_{91}\text{O}_2 + \text{CH}_3 \rightleftharpoons \text{PC}_4\text{H}_9\text{O} + \text{CH}_3\text{O}$	7.000e+12	0.000	-1000.00
$\text{C}_4\text{H}_{92}\text{O}_2 + \text{CH}_3 \rightleftharpoons \text{sC}_4\text{H}_9\text{O} + \text{CH}_3\text{O}$	7.000e+12	0.000	-1000.00
$\text{PC}_4\text{H}_9 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{PC}_4\text{H}_9\text{O} + \text{CH}_3\text{O}$	7.000e+12	0.000	-1000.00
$\text{sC}_4\text{H}_9 + \text{CH}_3\text{O}_2 \rightleftharpoons \text{sC}_4\text{H}_9\text{O} + \text{CH}_3\text{O}$	7.000e+12	0.000	-1000.00
$\text{C}_2\text{H}_4 + \text{CH}_3\text{O} \rightleftharpoons \text{C}_2\text{H}_3 + \text{CH}_3\text{OH}$	1.200e+11	0.000	6750.00
<i>Enhanced Collision. Efficiencies: REV = 1E+010, 0 = 9000</i>			
$\text{CH}_3\text{CO} + \text{H} \rightleftharpoons \text{CH}_2\text{CO} + \text{H}_2$	2.000e+13	0.000	0.00
<i>Enhanced Collision. Efficiencies: REV = 7.27E+009, 0 = 83040</i>			
$\text{CH}_3\text{CO} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{CO} + \text{CH}_4$	5.000e+13	0.000	0.00
<i>Enhanced Collision. Efficiencies: REV = 7.27E+009, 0 = 83040</i>			
$\text{C}_2\text{H}_6 + \text{CH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_2$	1.100e+14	0.000	-260.00
<i>Enhanced Collision. Efficiencies: REV = 3.829E+010, 0.56 = 440</i>			
$\text{OCHO} + \text{M} \rightleftharpoons \text{H} + \text{CO}_2 + \text{M}$	2.443e+15	-0.500	26500.00
<i>Enhanced Collision. Efficiencies: REV = 7.5E+013, 0 = 29000</i>			
$\text{iC}_3\text{H}_6\text{CO} + \text{OH} \rightleftharpoons \text{iC}_3\text{H}_7 + \text{CO}_2$	1.730e+12	0.000	-1010.00
<i>Enhanced Collision. Efficiencies: REV = 2.577E+014, -0.43 = 55480</i>			
$\text{iC}_3\text{H}_5\text{CHO} + \text{OH} \rightleftharpoons \text{iC}_3\text{H}_5\text{CO} + \text{H}_2\text{O}$	1.070e+13	0.000	-348.00
$\text{iC}_3\text{H}_5\text{CHO} + \text{HO}_2 \rightleftharpoons \text{iC}_3\text{H}_5\text{CO} + \text{H}_2\text{O}_2$	1.000e+12	0.000	11920.00
<i>Enhanced Collision. Efficiencies: REV = 3.756E+012, -0.33 = 12000</i>			
$\text{iC}_3\text{H}_5\text{CHO} + \text{CH}_3 \rightleftharpoons \text{iC}_3\text{H}_5\text{CO} + \text{CH}_4$	3.980e+12	0.000	8700.00
<i>Enhanced Collision. Efficiencies: REV = 1.519E+013, 0 = 25570</i>			
$\text{iC}_3\text{H}_5\text{CHO} + \text{O} \rightleftharpoons \text{iC}_3\text{H}_5\text{CO} + \text{OH}$	7.180e+12	0.000	1389.00
<i>Enhanced Collision. Efficiencies: REV = 4.608E+011, 0 = 15680</i>			
$\text{iC}_3\text{H}_5\text{CHO} + \text{O}_2 \rightleftharpoons \text{iC}_3\text{H}_5\text{CO} + \text{HO}_2$	2.000e+13	0.000	40700.00
<i>Enhanced Collision. Efficiencies: REV = 5.309E+010, 0.33 = -394</i>			

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$iC_3H_5CHO + H \rightleftharpoons iC_3H_5CO + H_2$	2.600e+12	0.000	2600.00
<i>Enhanced Collision. Efficiencies: REV = 3.799E+011, 0 = 18990</i>			
$C_2H_3COCH_3 + OH \rightleftharpoons CH_3CHO + CH_3CO$	1.370e+12	0.000	-1040.00
$iC_3H_6CO + H \rightleftharpoons iC_3H_7 + CO$	4.400e+12	0.000	1459.00
$iC_3H_6CO + O \rightleftharpoons CH_3COCH_3 + CO$	3.200e+12	0.000	-437.00
$C_2H_5CHCO + OH \rightleftharpoons NC_3H_7 + CO_2$	3.730e+12	0.000	-1010.00
$C_2H_5CHCO + H \rightleftharpoons NC_3H_7 + CO$	4.400e+12	0.000	1459.00
$C_2H_5CHCO + O \rightleftharpoons C_3H_6 + CO_2$	3.200e+12	0.000	-437.00
$CH_3CHCHO \rightleftharpoons C_2H_3CHO + H$	4.164e+12	-0.020	34210.00
<i>Enhanced Collision. Efficiencies: REV = 6.5E+012, 0 = 2900</i>			
$sC_3H_5CHO + HO_2 \rightleftharpoons sC_3H_5CO + H_2O_2$	1.000e+12	0.000	11920.00
<i>Enhanced Collision. Efficiencies: REV = 1.066E+013, -0.32 = 17890</i>			
$sC_3H_5CHO + CH_3 \rightleftharpoons sC_3H_5CO + CH_4$	3.980e+12	0.000	8700.00
<i>Enhanced Collision. Efficiencies: REV = 4.313E+013, 0.01 = 31460</i>			
$sC_3H_5CHO + O \rightleftharpoons sC_3H_5CO + OH$	7.180e+12	0.000	1389.00
<i>Enhanced Collision. Efficiencies: REV = 1.308E+012, 0.01 = 21570</i>			
$sC_3H_5CHO + O_2 \rightleftharpoons sC_3H_5CO + HO_2$	4.000e+13	0.000	37600.00
<i>Enhanced Collision. Efficiencies: REV = 3.014E+011, 0.34 = 2394</i>			
$sC_3H_5CHO + H \rightleftharpoons sC_3H_5CO + H_2$	2.600e+12	0.000	2600.00
<i>Enhanced Collision. Efficiencies: REV = 1.079E+012, 0.01 = 24880</i>			
$sC_3H_5CHO + OH \rightleftharpoons sC_3H_5CO + H_2O$	1.070e+13	0.000	-348.00
<i>Enhanced Collision. Efficiencies: REV = 1.922E+013, 0.01 = 37080</i>			
$sC_3H_5CO \rightleftharpoons C_3H_5 - s + CO$	8.600e+15	0.000	23000.00
<i>Enhanced Collision. Efficiencies: REV = 1E+011, 0 = 6000</i>			
$CH_3CHCOCH_3 \rightleftharpoons C_2H_3COCH_3 + H$	3.417e+16	-0.820	41770.00
<i>Enhanced Collision. Efficiencies: REV = 5E+012, 0 = 1200</i>			
$CH_3CHCOCH_3 \rightleftharpoons CH_3CHCO + CH_3$	1.406e+15	-0.440	38340.00
<i>Enhanced Collision. Efficiencies: REV = 1.23E+011, 0 = 7800</i>			
$iC_4H_5 + H \rightleftharpoons CH_3 + C_3H_3$	1.000e+14	0.000	0.00
$C_5H_5 \rightleftharpoons iC_5H_5$	3.900e+11	1.000	77180.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{IC}_5\text{H}_5 \rightleftharpoons \text{C}_3\text{H}_3 + \text{C}_2\text{H}_2$	3.700e+11	0.000	29830.00
$\text{C}_5\text{H}_5 + \text{O} \rightleftharpoons \text{NC}_4\text{H}_5 + \text{CO}$	1.000e+14	0.000	0.00
$\text{C}_5\text{H}_7 + \text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{CHCHO} + \text{CH}_2\text{O}$	1.700e+09	1.000	26400.00
$\text{C}_5\text{H}_7 + \text{O}_2 \rightleftharpoons \text{CH}_2\text{CHO} + \text{C}_2\text{H}_3\text{CHO}$	1.700e+09	1.000	26400.00
$\text{C}_5\text{H}_7 + \text{O} \rightleftharpoons \text{C}_2\text{H}_3\text{CHO} + \text{C}_2\text{H}_3$	2.000e+14	0.000	0.00
$\text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_5 + \text{O}_2$	1.312e+62	-14.784	49180.00
<i>Enhanced Collision. Efficiencies: REV = 2.876E+056, -13.82 = 14620</i>			
$\text{C}_2\text{H}_5\text{O}_2\text{H} \rightleftharpoons \text{CH}_3\text{CH}_2\text{O} + \text{OH}$	6.310e+14	0.000	42300.00
<i>Enhanced Collision. Efficiencies: REV = 5.661E+008, 1.033 = -1705</i>			
$\text{C}_2\text{H}_4\text{O}_{12} \rightleftharpoons \text{CH}_3 + \text{HCO}$	3.630e+13	0.000	57200.00
<i>Enhanced Collision. Efficiencies: REV = 10060, 1.549 = -2750</i>			
$\text{C}_2\text{H}_4\text{O}_{12} \rightleftharpoons \text{CH}_3\text{CHO}$	7.407e+12	0.000	53800.00
<i>Enhanced Collision. Efficiencies: REV = 9.013E+010, 0.207 = 80800</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{H}_2\text{O}$	1.780e+13	0.000	3610.00
<i>Enhanced Collision. Efficiencies: REV = 1.347E+010, 0.693 = 24740</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{H} \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{H}_2$	8.000e+13	0.000	9680.00
<i>Enhanced Collision. Efficiencies: REV = 5.71E+009, 0.799 = 15920</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{HO}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{H}_2\text{O}_2$	1.130e+13	0.000	30430.00
<i>Enhanced Collision. Efficiencies: REV = 4.666E+011, 0.104 = 20670</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{CH}_3\text{O}_2\text{H}$	1.130e+13	0.000	30430.00
<i>Enhanced Collision. Efficiencies: REV = 9.078E+012, -0.341 = 19070</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{C}_2\text{H}_5\text{O}_2 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{C}_2\text{H}_5\text{O}_2\text{H}$	1.130e+13	0.000	30430.00
<i>Enhanced Collision. Efficiencies: REV = 9.093E+012, -0.341 = 19080</i>			
$\text{C}_2\text{H}_4\text{O}_{12} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_3\text{O}_{12} + \text{CH}_4$	1.070e+12	0.000	11830.00
<i>Enhanced Collision. Efficiencies: REV = 6.967E+010, 0.353 = 19610</i>			
$\text{CH}_2\text{CCO} + \text{H} \rightleftharpoons \text{C}_2\text{H}_3\text{CO}$	8.000e+11	0.000	2000.00
$\text{CH}_2\text{CCO} + \text{OH} \Rightarrow \text{HCCCO} + \text{H}_2\text{O}$	2.200e+06	2.000	2780.00
$\text{CH}_2\text{CCO} + \text{H} \Rightarrow \text{HCCCO} + \text{H}_2$	8.200e+05	2.500	12280.00
$\text{HCCCO} + \text{O}_2 \Rightarrow \text{HCO} + \text{CO} + \text{CO}$	4.600e+16	-1.390	1010.00
$\text{CH}_2\text{CHCHCO} + \text{H} \rightleftharpoons \text{CO} + \text{C}_3\text{H}_5 - \text{A}$	1.100e+13	0.000	3400.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{CH}_2\text{CHCHCO} + \text{H} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HCCO}$	1.100e+13	0.000	3400.00
$\text{CH}_3 + \text{C}_2\text{H}_3\text{CO} \rightleftharpoons \text{C}_2\text{H}_5\text{CHCO}$	1.000e+13	0.000	0.00
$\text{CHOCH}_2\text{CHO} + \text{O}_2 \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{HO}_2$	4.000e+13	0.500	42200.00
$\text{CHOCH}_2\text{CHO} + \text{OH} \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{H}_2\text{O}$	5.400e+10	0.760	-340.00
$\text{CHOCH}_2\text{CHO} + \text{H} \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{H}_2$	8.000e+13	0.000	4200.00
$\text{CHOCH}_2\text{CHO} + \text{O} \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{OH}$	1.000e+13	0.000	1790.00
$\text{CHOCH}_2\text{CHO} + \text{HO}_2 \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{H}_2\text{O}_2$	5.600e+12	0.000	13600.00
$\text{CHOCH}_2\text{CHO} + \text{CH}_3\text{O} \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{CH}_3\text{OH}$	2.300e+11	0.000	1280.00
$\text{CHOCH}_2\text{CHO} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CHOCH}_2\text{CO} + \text{CH}_3\text{O}_2\text{H}$	2.000e+12	0.000	9500.00
$\text{CHOCH}_2\text{CO} \rightleftharpoons \text{CH}_2\text{CHO} + \text{CO}$	1.834e+15	-0.730	12910.00
$\text{C}_4\text{H}_8\text{CO} + \text{H} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CO}$	4.400e+12	0.000	1459.00
$\text{C}_4\text{H}_8\text{CO} + \text{OH} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{CO}_2$	3.730e+12	0.000	-1010.00
$\text{C}_4\text{H}_8\text{CO} + \text{O} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{CO}_2$	3.200e+12	0.000	-437.00
$\text{C}_4\text{H}_8\text{CO} + \text{O} \rightleftharpoons \text{C}_4\text{H}_7\text{CO} + \text{OH}$	8.800e+10	0.700	3250.00
$\text{C}_4\text{H}_8\text{CO} + \text{H} \rightleftharpoons \text{C}_4\text{H}_7\text{CO} + \text{H}_2$	5.400e+04	2.500	-1900.00
$\text{C}_4\text{H}_8\text{CO} + \text{OH} \rightleftharpoons \text{C}_4\text{H}_7\text{CO} + \text{H}_2\text{O}$	3.000e+06	2.000	-1520.00
$\text{C}_4\text{H}_8\text{CO} + \text{HO}_2 \rightleftharpoons \text{C}_4\text{H}_7\text{CO} + \text{H}_2\text{O}_2$	6.400e+03	2.600	12400.00
$\text{C}_4\text{H}_7\text{CO} \rightleftharpoons \text{C}_4\text{H}_7 - 1 + \text{CO}$	1.834e+15	-0.730	12910.00
$\text{EA} \rightleftharpoons \text{CH}_3\text{COOH} + \text{C}_2\text{H}_4$	2.000e+12	0.000	47290.00
$\text{EA}_{2j} + \text{H} (+ \text{M}) \rightleftharpoons \text{EA} (+ \text{M})$	1.000e+14	0.000	0.00
Low pressure limit	4.436e+125	-30.800	113950.00
Troie parameters: a=0.96, T***=9.9996E+009, T*=1.3439, T**=6.6987E+008			
$\text{EAEj} + \text{H} (+ \text{M}) \rightleftharpoons \text{EA} (+ \text{M})$	1.000e+14	0.000	0.00
Low pressure limit	1.325e+113	-27.260	114130.00
Troie parameters: a=0.084076, T***=3.6151, T*=9.9997E+009, T**=6.7101E+009			
$\text{EAMj} + \text{H} (+ \text{M}) \rightleftharpoons \text{EA} (+ \text{M})$	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troie parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
$\text{EA} (+ \text{M}) \rightleftharpoons \text{C}_2\text{H}_5\text{OCO} + \text{CH}_3 (+ \text{M})$	2.627e+27	-3.230	97690.00
Low pressure limit	7.718e+18	-0.270	71920.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
Troel parameters: a=0.632, T***=8.8245E+009, T*=1623.7, T**=7.5961E+007			
EA(+ M) $\rightleftharpoons$ CH ₃ CO + CH ₃ CH ₂ O(+ M)	1.650e+24	-2.040	100200.00
Low pressure limit	1.361e+16	0.760	78320.00
Troel parameters: a=0.74, T***=7.3301E+009, T*=2116.9, T**=6.7101E+009			
EA(+ M) $\rightleftharpoons$ CH ₃ CO ₂ + C ₂ H ₅ (+ M)	5.734e+25	-2.760	92110.00
Low pressure limit	9.712e+16	0.280	68840.00
Troel parameters: a=0.448, T***=1262.4, T*=4.6756E+009, T**=1.7861E+009			
EA + O ₂ $\rightleftharpoons$ EA ₂ j + HO ₂	2.000e+13	0.000	47300.00
EA + O ₂ $\rightleftharpoons$ EAEj + HO ₂	2.000e+13	0.000	48200.00
EA + O ₂ $\rightleftharpoons$ EAMj + HO ₂	3.000e+13	0.000	52290.00
EA + H $\rightleftharpoons$ EA ₂ j + H ₂	9.400e+04	2.750	6280.00
EA + H $\rightleftharpoons$ EAEj + H ₂	1.790e+05	2.530	3420.00
EA + H $\rightleftharpoons$ EAMj + H ₂	9.400e+04	2.750	6280.00
EA + O $\rightleftharpoons$ EA ₂ j + OH	9.650e+04	2.680	3716.00
EA + O $\rightleftharpoons$ EAEj + OH	1.450e+05	2.470	880.00
EA + O $\rightleftharpoons$ EAMj + OH	9.650e+04	2.680	3716.00
EA + OH $\rightleftharpoons$ EA ₂ j + H ₂ O	5.250e+09	0.970	1590.00
EA + OH $\rightleftharpoons$ EAEj + H ₂ O	1.306e+05	2.430	-1457.00
EA + OH $\rightleftharpoons$ EAMj + H ₂ O	5.250e+09	0.970	1590.00
EA + CH ₃ $\rightleftharpoons$ EA ₂ j + CH ₄	4.520e-01	3.650	7154.00
EA + CH ₃ $\rightleftharpoons$ EAEj + CH ₄	1.990e+01	3.370	7635.00
EA + CH ₃ $\rightleftharpoons$ EAMj + CH ₄	4.520e-01	3.650	7154.00
EA + HO ₂ $\rightleftharpoons$ EA ₂ j + H ₂ O ₂	8.400e+12	0.000	20440.00
EA + HO ₂ $\rightleftharpoons$ EAEj + H ₂ O ₂	3.610e+03	2.550	10530.00
EA + HO ₂ $\rightleftharpoons$ EAMj + H ₂ O ₂	8.400e+12	0.000	20440.00
EA + CH ₃ O ₂ $\rightleftharpoons$ EA ₂ j + CH ₃ O ₂ H	8.400e+12	0.000	20440.00
EA + CH ₃ O ₂ $\rightleftharpoons$ EAEj + CH ₃ O ₂ H	7.220e+03	2.550	10530.00
EA + CH ₃ O ₂ $\rightleftharpoons$ EAMj + CH ₃ O ₂ H	8.400e+12	0.000	20440.00
EA + CH ₃ O $\rightleftharpoons$ EA ₂ j + CH ₃ OH	1.581e+11	0.000	7000.00
EA + CH ₃ O $\rightleftharpoons$ EAEj + CH ₃ OH	4.580e+10	0.000	2873.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
EA + CH ₃ O $\rightleftharpoons$ EAMj + CH ₃ OH	1.581e+11	0.000	7000.00
EA ₂ j $\rightleftharpoons$ EAMj	1.481e+08	1.000	24500.00
EA ₂ j $\rightleftharpoons$ EAEj	5.746e+08	1.000	18000.00
EA ₂ j + O ₂ $\rightleftharpoons$ EA ₂ OO	1.000e+18	-2.500	0.00
EAEj + O ₂ $\rightleftharpoons$ EAEEO	1.200e+10	0.000	-2300.00
EAMj + O ₂ $\rightleftharpoons$ EAMOO	9.000e+18	-2.500	0.00
EAEEO $\rightleftharpoons$ EAEed + HO ₂	5.075e+42	-9.410	42490.00
EAMOO $\rightleftharpoons$ EAEed + HO ₂	5.044e+38	-8.110	41490.00
EA ₂ j $\rightleftharpoons$ CH ₂ CO + CH ₃ CH ₂ O	1.460e+12	0.610	53276.00
EAEj $\rightleftharpoons$ CH ₃ CHO + CH ₃ CO	1.127e+21	-1.730	42550.00
EAMj $\rightleftharpoons$ C ₂ H ₄ + CH ₃ CO ₂	1.340e+13	-0.400	24610.00
EAEj $\rightleftharpoons$ EAEed + H	3.000e+13	0.000	39000.00
EAMj $\rightleftharpoons$ EAEed + H	3.000e+13	0.000	38000.00
EAEed + OH $\rightleftharpoons$ CH ₃ CHO + CH ₃ CO ₂	1.370e+12	0.000	-1040.00
HOCO $\rightleftharpoons$ CO + OH	1.186e+14	0.130	36460.00
HOCO $\rightleftharpoons$ CO ₂ + H	8.220e+11	0.410	35340.00
EP $\rightleftharpoons$ C ₂ H ₅ COOH + C ₂ H ₄	2.000e+12	0.000	47290.00
EP ₃ j + H(+ M) $\rightleftharpoons$ EP(+ M)	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troce parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
EP ₂ j + H(+ M) $\rightleftharpoons$ EP(+ M)	1.000e+14	0.000	0.00
Low pressure limit	4.436e+125	-30.800	113950.00
Troce parameters: a=0.96, T***=9.9996E+009, T*=1.3439, T**=6.6987E+008			
EPEj + H(+ M) $\rightleftharpoons$ EP(+ M)	1.000e+14	0.000	0.00
Low pressure limit	1.325e+113	-27.260	114130.00
Troce parameters: a=0.084076, T***=3.6151, T*=9.9997E+009, T**=6.7101E+009			
EPMj + H(+ M) $\rightleftharpoons$ EP(+ M)	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troce parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
EP(+ M) $\rightleftharpoons$ EA ₂ j + CH ₃ (+ M)	5.732e+23	-2.330	87740.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
Low pressure limit	4.352e+14	0.820	63570.00
Troe parameters: a=0.169, T***=5712.9, T*=40.466, T**=6.7101E+009			
EP(+ M) $\rightleftharpoons$ C ₂ H ₅ OCO + C ₂ H ₅ (+ M)	2.627e+27	-3.230	94690.00
Low pressure limit	7.718e+18	-0.270	71920.00
Troe parameters: a=0.632, T***=8.8245E+009, T*=1623.7, T**=7.5961E+007			
EP(+ M) $\rightleftharpoons$ C ₂ H ₅ CO + CH ₃ CH ₂ O(+ M)	1.650e+24	-2.040	100200.00
Low pressure limit	1.361e+16	0.760	78320.00
Troe parameters: a=0.74, T***=7.3301E+009, T*=2116.9, T**=6.7101E+009			
EP(+ M) $\rightleftharpoons$ C ₂ H ₅ CO ₂ + C ₂ H ₅ (+ M)	5.734e+25	-2.760	92110.00
Low pressure limit	9.712e+16	0.280	68840.00
Troe parameters: a=0.448, T***=1262.4, T*=4.6756E+009, T**=1.7861E+009			
EP(+ M) $\rightleftharpoons$ MPMj + CH ₃ (+ M)	3.388e+21	-1.580	92090.00
Low pressure limit	5.674e+12	1.460	68820.00
Troe parameters: a=0.406, T***=1523.5, T*=4.8431E+009, T**=9.3301E+009			
EP + O ₂ $\rightleftharpoons$ EP ₃ j + HO ₂	3.000e+13	0.000	52290.00
EP + O ₂ $\rightleftharpoons$ EP ₂ j + HO ₂	2.000e+13	0.000	44300.00
EP + O ₂ $\rightleftharpoons$ EPEj + HO ₂	2.000e+13	0.000	48200.00
EP + O ₂ $\rightleftharpoons$ EPMj + HO ₂	3.000e+13	0.000	52290.00
EP + H $\rightleftharpoons$ EP ₃ j + H ₂	9.400e+04	2.750	6280.00
EP + H $\rightleftharpoons$ EP ₂ j + H ₂	1.300e+06	2.400	4471.00
EP + H $\rightleftharpoons$ EPEj + H ₂	1.790e+05	2.530	3420.00
EP + H $\rightleftharpoons$ EPMj + H ₂	9.400e+04	2.750	6280.00
EP + O $\rightleftharpoons$ EP ₃ j + OH	9.650e+04	2.680	3716.00
EP + O $\rightleftharpoons$ EP ₂ j + OH	4.770e+04	2.710	2106.00
EP + O $\rightleftharpoons$ EPEj + OH	1.450e+05	2.470	880.00
EP + O $\rightleftharpoons$ EPMj + OH	9.650e+04	2.680	3716.00
EP + OH $\rightleftharpoons$ EP ₃ j + H ₂ O	5.250e+09	0.970	1590.00
EP + OH $\rightleftharpoons$ EP ₂ j + H ₂ O	4.680e+07	1.610	-35.00
EP + OH $\rightleftharpoons$ EPEj + H ₂ O	1.306e+05	2.430	-1457.00
EP + OH $\rightleftharpoons$ EPMj + H ₂ O	5.250e+09	0.970	1590.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{EP} + \text{CH}_3 \rightleftharpoons \text{EP}_3\text{j} + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{EP} + \text{CH}_3 \rightleftharpoons \text{EP}_2\text{j} + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{EP} + \text{CH}_3 \rightleftharpoons \text{EPEj} + \text{CH}_4$	1.990e+01	3.370	7635.00
$\text{EP} + \text{CH}_3 \rightleftharpoons \text{EPMj} + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{EP} + \text{HO}_2 \rightleftharpoons \text{EP}_3\text{j} + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{EP} + \text{HO}_2 \rightleftharpoons \text{EP}_2\text{j} + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{EP} + \text{HO}_2 \rightleftharpoons \text{EPEj} + \text{H}_2\text{O}_2$	3.610e+03	2.550	10530.00
$\text{EP} + \text{HO}_2 \rightleftharpoons \text{EPMj} + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{EP} + \text{CH}_3\text{O} \rightleftharpoons \text{EP}_3\text{j} + \text{CH}_3\text{OH}$	1.581e+11	0.000	7000.00
$\text{EP} + \text{CH}_3\text{O} \rightleftharpoons \text{EP}_2\text{j} + \text{CH}_3\text{OH}$	1.095e+11	0.000	5000.00
$\text{EP} + \text{CH}_3\text{O} \rightleftharpoons \text{EPEj} + \text{CH}_3\text{OH}$	4.580e+10	0.000	2873.00
$\text{EP} + \text{CH}_3\text{O} \rightleftharpoons \text{EPMj} + \text{CH}_3\text{OH}$	1.581e+11	0.000	7000.00
$\text{EP} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EP}_3\text{j} + \text{CH}_3\text{O}_2\text{H}$	8.400e+12	0.000	20440.00
$\text{EP} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EP}_2\text{j} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00
$\text{EP} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPEj} + \text{CH}_3\text{O}_2\text{H}$	7.220e+03	2.550	10530.00
$\text{EP} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPMj} + \text{CH}_3\text{O}_2\text{H}$	8.400e+12	0.000	20440.00
$\text{EP}_3\text{j} \rightleftharpoons \text{EPEj}$	9.872e+07	1.000	20000.00
$\text{EP}_3\text{j} \rightleftharpoons \text{EPMj}$	2.544e+07	1.000	24700.00
$\text{EP}_2\text{j} \rightleftharpoons \text{EPMj}$	1.481e+08	1.000	24500.00
$\text{EP}_2\text{j} \rightleftharpoons \text{EPEj}$	5.746e+08	1.000	18000.00
$\text{EP}_3\text{j} + \text{O}_2 \rightleftharpoons \text{EP}_3\text{OO}$	9.000e+18	-2.500	0.00
$\text{EP}_2\text{j} + \text{O}_2 \rightleftharpoons \text{EP}_2\text{OO}$	9.000e+18	-2.500	0.00
$\text{EPEj} + \text{O}_2 \rightleftharpoons \text{EPEOO}$	1.200e+10	0.000	-2300.00
$\text{EPMj} + \text{O}_2 \rightleftharpoons \text{EPMOO}$	9.000e+18	-2.500	0.00
$\text{EP}_3\text{OO} \rightleftharpoons \text{EP}_2\text{d} + \text{HO}_2$	5.044e+38	-8.110	41490.00
$\text{EP}_2\text{OO} \rightleftharpoons \text{EP}_2\text{d} + \text{HO}_2$	5.075e+42	-9.410	42490.00
$\text{EPEOO} \rightleftharpoons \text{EPEd} + \text{HO}_2$	5.075e+42	-9.410	42490.00
$\text{EPMOO} \rightleftharpoons \text{EPEd} + \text{HO}_2$	5.044e+38	-8.110	41490.00
$\text{EP}_3\text{j} \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{OCO}$	3.030e+13	0.270	34667.00
$\text{EP}_2\text{j} \rightleftharpoons \text{CH}_3\text{CHCO} + \text{CH}_3\text{CH}_2\text{O}$	1.460e+12	0.610	53276.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{EPEj} \rightleftharpoons \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{CO}$	1.127e+21	-1.730	42550.00
$\text{EPMj} \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_2\text{H}_5\text{CO}_2$	1.340e+13	-0.400	24610.00
$\text{MPMj} \rightleftharpoons \text{CH}_2\text{O} + \text{C}_2\text{H}_5\text{CO}$	1.230e+13	0.375	36714.00
$\text{EP}_{3j} \cdot \text{O} \Rightarrow \text{EA}_{2j} + \text{CO}$	1.834e+15	-0.730	12910.00
$\text{EP}_{3j_2} \cdot \text{O} \rightleftharpoons \text{CH}_2\text{CO} + \text{C}_2\text{H}_5\text{OCO}$	1.230e+13	0.375	36714.00
$\text{EP}_{3j} \rightleftharpoons \text{EP}_2\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EP}_{2j} \rightleftharpoons \text{EP}_2\text{d} + \text{H}$	3.000e+13	0.000	39000.00
$\text{EPEj} \rightleftharpoons \text{EPEd} + \text{H}$	3.000e+13	0.000	39000.00
$\text{EPMj} \rightleftharpoons \text{EPEd} + \text{H}$	3.000e+13	0.000	38000.00
$\text{C}_2\text{H}_5\text{COOH} \rightleftharpoons \text{CH}_3\text{CHCO} + \text{H}_2\text{O}$	4.470e+14	0.000	79890.00
$\text{C}_2\text{H}_5\text{COOH} \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO}_2$	7.080e+13	0.000	74520.00
$\text{C}_2\text{H}_5\text{COOH} \Rightarrow \text{C}_2\text{H}_5\text{CO} + \text{OH}$	1.400e+17	0.000	105815.70
$\text{C}_2\text{H}_5\text{COOH} \Rightarrow \text{C}_2\text{H}_5\text{CO}_2 + \text{H}$	2.300e+14	0.000	106345.30
$\text{C}_2\text{H}_5\text{COOH} \Rightarrow \text{C}_2\text{H}_5 + \text{HOCO}$	8.200e+16	0.000	88817.00
$\text{C}_2\text{H}_5\text{COOH} \Rightarrow \text{CH}_3 + \text{CH}_2\text{COOH}$	2.900e+16	0.000	81917.10
$\text{C}_2\text{H}_5\text{COOH} + \text{H} \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2$	9.400e+04	2.750	6280.00
$\text{C}_2\text{H}_5\text{COOH} + \text{H} \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{H}_2$	1.300e+06	2.400	4471.00
$\text{C}_2\text{H}_5\text{COOH} + \text{H} \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2 + \text{H}_2$	5.550e-23	10.600	-4459.00
$\text{C}_2\text{H}_5\text{COOH} + \text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{OH}$	9.650e+04	2.680	3716.00
$\text{C}_2\text{H}_5\text{COOH} + \text{O} \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{OH}$	4.770e+04	2.710	2106.00
$\text{C}_2\text{H}_5\text{COOH} + \text{O} \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2 + \text{OH}$	1.460e-03	4.730	1727.00
$\text{C}_2\text{H}_5\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}$	5.250e+09	0.970	1590.00
$\text{C}_2\text{H}_5\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{H}_2\text{O}$	4.680e+07	1.610	-35.00
$\text{C}_2\text{H}_5\text{COOH} + \text{OH} \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2 + \text{H}_2\text{O}$	2.810e+02	2.970	-580.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3 \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3 \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3 \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2 + \text{CH}_4$	2.035e+00	3.570	7722.00
$\text{C}_2\text{H}_5\text{COOH} + \text{HO}_2 \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{C}_2\text{H}_5\text{COOH} + \text{HO}_2 \Rightarrow \text{CH}_3\text{CHOCHO} + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{C}_2\text{H}_5\text{COOH} + \text{HO}_2 \rightleftharpoons \text{C}_2\text{H}_5\text{CO}_2 + \text{H}_2\text{O}_2$	2.500e+12	0.000	24000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{O}_2\text{H}$	8.400e+12	0.000	20440.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_2\text{CH}_2\text{COOH} + \text{CH}_3\text{OH}$	1.581e+11	0.000	7000.00
$\text{C}_2\text{H}_5\text{COOH} + \text{CH}_3\text{O} \rightleftharpoons \text{CH}_3\text{CHOCHO} + \text{CH}_3\text{OH}$	1.095e+11	0.000	5000.00
$\text{CH}_2\text{CH}_2\text{COOH} + \text{M} \rightleftharpoons \text{C}_2\text{H}_4 + \text{HOCO} + \text{M}$	3.030e+16	0.270	34667.00
$\text{CH}_2\text{CH}_2\text{COOH} \rightleftharpoons \text{C}_2\text{H}_3\text{COOH} + \text{H}$	3.200e+13	0.000	34800.00
$\text{CH}_3\text{CHOCHO} \rightleftharpoons \text{CH}_3\text{CHCO} + \text{OH}$	3.046e+21	-1.610	57300.00
$\text{CH}_3\text{CHOCHO} \rightleftharpoons \text{C}_2\text{H}_3\text{COOH} + \text{H}$	3.000e+13	0.000	51500.00
$\text{CH}_3\text{CHOCHO} \Rightarrow \text{CO}_2 + \text{C}_2\text{H}_5$	1.700e+09	1.000	38640.00
$\text{C}_2\text{H}_3\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{CH}_2\text{COOH}$	1.370e+12	0.000	-1040.00
$\text{C}_2\text{H}_3\text{COOH} + \text{OH} \rightleftharpoons \text{CH}_3 + \text{HCO} + \text{HOCO}$	1.370e+12	0.000	-1040.00
$\text{C}_2\text{H}_3\text{COOH} \rightleftharpoons \text{C}_2\text{H}_3 + \text{HOCO}$	3.752e+21	-1.890	112900.00
$\text{C}_2\text{H}_3\text{COOH} \rightleftharpoons \text{C}_2\text{H}_3\text{CO} + \text{OH}$	5.206e+20	-1.160	100900.00
$\text{C}_2\text{H}_3\text{COOH} \rightleftharpoons \text{C}_2\text{H}_4 + \text{CO}_2$	7.080e+13	0.000	74520.00
$\text{C}_2\text{H}_3\text{COOH} + \text{H} \rightleftharpoons \text{H}_2 + \text{CO}_2 + \text{C}_2\text{H}_3$	4.200e+06	2.100	6900.00
$\text{C}_2\text{H}_3\text{COOH} + \text{OH} \rightleftharpoons \text{H}_2\text{O} + \text{CO}_2 + \text{C}_2\text{H}_3$	5.400e+04	2.000	-340.00
$\text{C}_2\text{H}_3\text{COOH} + \text{HO}_2 \rightleftharpoons \text{H}_2\text{O}_2 + \text{CO}_2 + \text{C}_2\text{H}_3$	1.000e+11	0.000	11500.00
$\text{C}_2\text{H}_3\text{COOH} + \text{CH}_3 \rightleftharpoons \text{CH}_4 + \text{CO}_2 + \text{C}_2\text{H}_3$	1.400e+01	3.100	9940.00
$\text{C}_2\text{H}_3\text{COOH} + \text{C}_2\text{H}_5 \rightleftharpoons \text{C}_2\text{H}_6 + \text{CO}_2 + \text{C}_2\text{H}_3$	1.400e+01	3.100	8940.00
$\text{EP}_2\text{d} + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{EA}_2\text{j}$	1.370e+12	0.000	-1040.00
$\text{EPed} + \text{OH} \rightleftharpoons \text{CH}_2\text{O} + \text{MPMj}$	1.370e+12	0.000	-1040.00
$\text{EPed} + \text{OH} \rightleftharpoons \text{CH}_3\text{CHO} + \text{C}_2\text{H}_5\text{CO}_2$	1.370e+12	0.000	-1040.00
$\text{EP}_2\text{d} \rightleftharpoons \text{C}_2\text{H}_3\text{COOH} + \text{C}_2\text{H}_4$	2.000e+12	0.000	47290.00
$\text{EP}_3 \cdot \text{O} + \text{H} \rightleftharpoons \text{EP}_3\text{j} \cdot \text{O} + \text{H}_2$	1.200e+14	0.000	7000.00
$\text{EP}_3 \cdot \text{O} + \text{O} \rightleftharpoons \text{EP}_3\text{j} \cdot \text{O} + \text{OH}$	5.850e+12	0.000	1808.00
$\text{EP}_3 \cdot \text{O} + \text{OH} \rightleftharpoons \text{EP}_3\text{j} \cdot \text{O} + \text{H}_2\text{O}$	2.650e+12	0.000	-730.00
$\text{EP}_3 \cdot \text{O} + \text{HO}_2 \rightleftharpoons \text{EP}_3\text{j} \cdot \text{O} + \text{H}_2\text{O}_2$	1.700e+12	0.000	10700.00
$\text{C}_3\text{H}_7\text{COOH} \rightleftharpoons \text{C}_2\text{H}_5\text{CHCO} + \text{H}_2\text{O}$	4.470e+14	0.000	79890.00
$\text{C}_3\text{H}_7\text{COOH} \rightleftharpoons \text{C}_3\text{H}_8 + \text{CO}_2$	7.080e+13	0.000	74520.00
$\text{C}_3\text{H}_7\text{COOH} \rightleftharpoons \text{NC}_3\text{H}_7\text{CO} + \text{OH}$	1.400e+17	0.000	105815.70

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_3H_7COOH \Rightarrow C_3H_7CO_2 + H$	2.300e+14	0.000	106345.30
$C_3H_7COOH \Rightarrow NC_3H_7 + HOCO$	8.200e+16	0.000	88817.00
$C_3H_7COOH \Rightarrow C_2H_5 + CH_2COOH$	2.900e+16	0.000	78917.10
$C_3H_7COOH \Rightarrow CH_3 + CH_2CH_2COOH$	1.700e+17	0.000	87662.10
$C_3H_7COOH + H \rightleftharpoons C_3H_7CO_2 + H_2$	5.550e-23	10.600	-4459.00
$C_3H_7COOH + O \rightleftharpoons C_3H_7CO_2 + OH$	1.460e-03	4.730	1727.00
$C_3H_7COOH + OH \rightleftharpoons C_3H_7CO_2 + H_2O$	2.810e+02	2.970	-580.00
$C_3H_7COOH + CH_3 \rightleftharpoons C_3H_7CO_2 + CH_4$	2.035e+00	3.570	7722.00
$C_3H_7COOH + HO_2 \rightleftharpoons C_3H_7CO_2 + H_2O_2$	2.500e+12	0.000	24000.00
$C_3H_7CO_2 + M \rightleftharpoons NC_3H_7 + CO_2 + M$	4.400e+15	0.000	10500.00
$C_3H_5COOH + OH \Rightarrow CH_2O + CH_2CH_2COOH$	1.370e+12	0.000	-1040.00
$C_3H_5COOH + OH \Rightarrow CH_3CHO + CH_2COOH$	1.370e+12	0.000	-1040.00
$C_3H_5COOH + H \Rightarrow H_2 + CO_2 + C_3H_5 - s$	4.200e+06	2.100	6900.00
$C_3H_5COOH + OH \Rightarrow H_2O + CO_2 + C_3H_5 - s$	5.400e+04	2.000	-340.00
$C_3H_5COOH + HO_2 \Rightarrow H_2O_2 + CO_2 + C_3H_5 - s$	1.000e+11	0.000	11500.00
$C_3H_5COOH + CH_3 \Rightarrow CH_4 + CO_2 + C_3H_5 - s$	1.400e+01	3.100	9940.00
$C_3H_5COOH + C_2H_5 \Rightarrow C_2H_6 + CO_2 + C_3H_5 - s$	1.400e+01	3.100	8940.00
$EPE \rightleftharpoons C_4H_9COOH + C_2H_4$	2.000e+12	0.000	47290.00
$EPE_{5j} + H(+ M) \rightleftharpoons EPE(+ M)$	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troel parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
$EPE_{4j} + H(+ M) \rightleftharpoons EPE(+ M)$	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troel parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
$EPE_{3j} + H(+ M) \rightleftharpoons EPE(+ M)$	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troel parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
$EPE_{2j} + H(+ M) \rightleftharpoons EPE(+ M)$	1.000e+14	0.000	0.00
Low pressure limit	4.436e+125	-30.800	113950.00
Troel parameters: a=0.96, T***=9.9996E+009, T*=1.3439, T**=6.6987E+008			

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
EPEEj + H(+ M) $\rightleftharpoons$ EPE(+ M)	1.000e+14	0.000	0.00
Low pressure limit	1.325e+113	-27.260	114130.00
Troel parameters: a=0.084076, T***=3.6151, T*=9.9997E+009, T**=6.7101E+009			
EPEMj + H(+ M) $\rightleftharpoons$ EPE(+ M)	1.000e+14	0.000	0.00
Low pressure limit	9.742e+103	-24.610	115380.00
Troel parameters: a=0.872, T***=9.99E+009, T*=29.264, T**=7.5961E+007			
EPE(+ M) $\rightleftharpoons$ EP ₃ j + C ₂ H ₅ (+ M)	5.732e+23	-2.330	87740.00
Low pressure limit	4.352e+14	0.820	63570.00
Troel parameters: a=0.169, T***=5712.9, T*=40.466, T**=6.7101E+009			
EPE(+ M) $\rightleftharpoons$ EA ₂ j + NC ₃ H ₇ (+ M)	2.700e+22	-1.860	85680.00
Low pressure limit	3.910e+74	-16.420	83700.00
Troel parameters: a=0.8698, T***=7.499E+009, T*=1.6303, T**=7.596E+007			
EPE(+ M) $\rightleftharpoons$ C ₂ H ₅ OCO + PC ₄ H ₉ (+ M)	2.627e+27	-3.230	94690.00
Low pressure limit	7.718e+18	-0.270	71920.00
Troel parameters: a=0.632, T***=8.8245E+009, T*=1623.7, T**=7.5961E+007			
EPE(+ M) $\rightleftharpoons$ NC ₄ H ₉ CO + CH ₃ CH ₂ O(+ M)	1.650e+24	-2.040	100200.00
Low pressure limit	1.361e+16	0.760	78320.00
Troel parameters: a=0.74, T***=7.3301E+009, T*=2116.9, T**=6.7101E+009			
EPE(+ M) $\rightleftharpoons$ C ₄ H ₉ CO ₂ + C ₂ H ₅ (+ M)	5.734e+25	-2.760	92110.00
Low pressure limit	9.712e+16	0.280	68840.00
Troel parameters: a=0.448, T***=1262.4, T*=4.6756E+009, T**=1.7861E+009			
EPE + O ₂ $\rightleftharpoons$ EPE ₅ j + HO ₂	3.000e+13	0.000	52290.00
EPE + O ₂ $\rightleftharpoons$ EPE ₄ j + HO ₂	4.000e+13	0.000	47690.00
EPE + O ₂ $\rightleftharpoons$ EPE ₃ j + HO ₂	4.000e+13	0.000	47690.00
EPE + O ₂ $\rightleftharpoons$ EPE ₂ j + HO ₂	2.000e+13	0.000	44300.00
EPE + O ₂ $\rightleftharpoons$ EPEEj + HO ₂	2.000e+13	0.000	48200.00
EPE + O ₂ $\rightleftharpoons$ EPEMj + HO ₂	3.000e+13	0.000	52290.00
EPE + H $\rightleftharpoons$ EPE ₅ j + H ₂	9.400e+04	2.750	6280.00
EPE + H $\rightleftharpoons$ EPE ₄ j + H ₂	1.300e+06	2.400	4471.00
EPE + H $\rightleftharpoons$ EPE ₃ j + H ₂	1.300e+06	2.400	4471.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{EPE} + \text{H} \rightleftharpoons \text{EPE}_2\text{j} + \text{H}_2$	1.300e+06	2.400	4471.00
$\text{EPE} + \text{H} \rightleftharpoons \text{EPEEj} + \text{H}_2$	1.794e+05	2.530	3420.00
$\text{EPE} + \text{H} \rightleftharpoons \text{EPEMj} + \text{H}_2$	9.400e+04	2.750	6280.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPE}_5\text{j} + \text{OH}$	9.650e+04	2.680	3716.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPE}_4\text{j} + \text{OH}$	4.770e+04	2.710	2106.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPE}_3\text{j} + \text{OH}$	4.770e+04	2.710	2106.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPE}_2\text{j} + \text{OH}$	4.770e+04	2.710	2106.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPEEj} + \text{OH}$	1.450e+05	2.410	876.00
$\text{EPE} + \text{O} \rightleftharpoons \text{EPEMj} + \text{OH}$	9.650e+04	2.680	3716.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPE}_5\text{j} + \text{H}_2\text{O}$	5.250e+09	0.970	1590.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPE}_4\text{j} + \text{H}_2\text{O}$	4.680e+07	1.610	-35.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPE}_3\text{j} + \text{H}_2\text{O}$	4.680e+07	1.610	-35.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPE}_2\text{j} + \text{H}_2\text{O}$	4.680e+07	1.610	-35.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPEEj} + \text{H}_2\text{O}$	1.306e+05	2.430	-1457.00
$\text{EPE} + \text{OH} \rightleftharpoons \text{EPEMj} + \text{H}_2\text{O}$	5.250e+09	0.970	1590.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPE}_5\text{j} + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPE}_4\text{j} + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPE}_3\text{j} + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPE}_2\text{j} + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPEEj} + \text{CH}_4$	1.990e+01	3.370	7635.00
$\text{EPE} + \text{CH}_3 \rightleftharpoons \text{EPEMj} + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPE}_5\text{j} + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPE}_4\text{j} + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPE}_3\text{j} + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPE}_2\text{j} + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPEEj} + \text{H}_2\text{O}_2$	3.610e+03	2.550	10530.00
$\text{EPE} + \text{HO}_2 \rightleftharpoons \text{EPEMj} + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPE}_5\text{j} + \text{CH}_3\text{O}_2\text{H}$	8.400e+12	0.000	20440.00
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPE}_4\text{j} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPE}_3\text{j} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPE}_2\text{j} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPEEj} + \text{CH}_3\text{O}_2\text{H}$	5.600e+12	0.000	17690.00
$\text{EPE} + \text{CH}_3\text{O}_2 \rightleftharpoons \text{EPEMj} + \text{CH}_3\text{O}_2\text{H}$	8.400e+12	0.000	20440.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPE}_5\text{j} + \text{CH}_3\text{OH}$	1.581e+11	0.000	7000.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPE}_4\text{j} + \text{CH}_3\text{OH}$	1.095e+11	0.000	5000.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPE}_3\text{j} + \text{CH}_3\text{OH}$	1.095e+11	0.000	5000.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPE}_2\text{j} + \text{CH}_3\text{OH}$	1.095e+11	0.000	5000.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPEEj} + \text{CH}_3\text{OH}$	4.580e+10	0.000	2873.00
$\text{EPE} + \text{CH}_3\text{O} \rightleftharpoons \text{EPEMj} + \text{CH}_3\text{OH}$	1.581e+11	0.000	7000.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{EPE}_5\text{j}$	8.619e+08	1.000	19800.00
$\text{EPE}_4\text{j} \rightleftharpoons \text{EPEEj}$	1.696e+07	1.000	20200.00
$\text{EPE}_3\text{j} \rightleftharpoons \text{EPEEj}$	9.872e+07	1.000	20000.00
$\text{EPE}_3\text{j} \rightleftharpoons \text{EPEMj}$	2.544e+07	1.000	24700.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{EPEEj}$	5.746e+08	1.000	18000.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{EPEMj}$	1.481e+08	1.000	24500.00
$\text{EPE}_5\text{j} \rightleftharpoons \text{C}_2\text{H}_4 + \text{EP}_3\text{j}$	2.000e+13	0.000	28700.00
$\text{EPE}_4\text{j} + \text{M} \rightleftharpoons \text{C}_3\text{H}_6 + \text{EA}_2\text{j} + \text{M}$	5.250e+11	0.500	26591.00
$\text{EPE}_3\text{j} \rightleftharpoons \text{C}_4\text{H}_8 - 1 + \text{C}_2\text{H}_5\text{OCO}$	2.000e+13	0.000	31000.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{C}_4\text{H}_8\text{CO} + \text{CH}_3\text{CH}_2\text{O}$	1.460e+12	0.610	53276.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{C}_2\text{H}_5 + \text{EP}_2\text{d}$	2.000e+13	0.000	37000.00
$\text{EPEEj} \rightleftharpoons \text{CH}_3\text{CHO} + \text{NC}_4\text{H}_9\text{CO}$	1.127e+21	-1.73	42550.00
$\text{EPEMj} \rightleftharpoons \text{C}_2\text{H}_4 + \text{C}_4\text{H}_9\text{CO}_2$	2.000e+13	0.000	28000.00
$\text{EPE}_5\text{j} \rightleftharpoons \text{EPE}_4\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EPE}_4\text{j} \rightleftharpoons \text{EPE}_4\text{d} + \text{H}$	3.000e+13	0.000	39000.00
$\text{EPE}_4\text{j} \rightleftharpoons \text{EPE}_3\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EPE}_3\text{j} \rightleftharpoons \text{EPE}_3\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EPE}_3\text{j} \rightleftharpoons \text{EPE}_2\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EPE}_2\text{j} \rightleftharpoons \text{EPE}_2\text{d} + \text{H}$	3.000e+13	0.000	38000.00
$\text{EPEEj} \rightleftharpoons \text{EPEEd} + \text{H}$	3.000e+13	0.000	39000.00
$\text{EPEMj} \rightleftharpoons \text{EPEEd} + \text{H}$	3.000e+13	0.000	38000.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{C}_4\text{H}_9\text{COOH} \rightleftharpoons \text{C}_4\text{H}_8\text{CO} + \text{H}_2\text{O}$	4.470e+14	0.000	79890.00
$\text{C}_4\text{H}_9\text{COOH} \rightleftharpoons \text{NC}_4\text{H}_{10} + \text{CO}_2$	7.080e+13	0.000	74520.00
$\text{C}_4\text{H}_9\text{COOH} + \text{M} \rightleftharpoons \text{NC}_4\text{H}_9\text{CO} + \text{OH} + \text{M}$	1.400e+17	0.000	105815.70
$\text{C}_4\text{H}_9\text{COOH} + \text{M} \rightleftharpoons \text{C}_4\text{H}_9\text{CO}_2 + \text{H} + \text{M}$	2.300e+14	0.000	106345.30
$\text{C}_4\text{H}_9\text{COOH} \rightleftharpoons \text{PC}_4\text{H}_9 + \text{HOCO}$	8.200e+16	0.000	88817.00
$\text{C}_4\text{H}_9\text{COOH} \rightleftharpoons \text{NC}_3\text{H}_7 + \text{CH}_2\text{COOH}$	2.900e+16	0.000	78917.10
$\text{C}_4\text{H}_9\text{COOH} \rightleftharpoons \text{C}_2\text{H}_5 + \text{CH}_2\text{CH}_2\text{COOH}$	1.700e+17	0.000	87662.10
$\text{C}_4\text{H}_9\text{COOH} + \text{H} \rightleftharpoons \text{BuCOOH} - 5 + \text{H}_2$	9.400e+04	2.750	6280.00
$\text{C}_4\text{H}_9\text{COOH} + \text{H} \rightleftharpoons \text{BuCOOH} - 4 + \text{H}_2$	1.040e+07	2.400	4471.00
$\text{C}_4\text{H}_9\text{COOH} + \text{H} \rightleftharpoons \text{BuCOOH} - 3 + \text{H}_2$	7.800e+06	2.400	4471.00
$\text{C}_4\text{H}_9\text{COOH} + \text{H} \rightleftharpoons \text{BuCOOH} - 2 + \text{H}_2$	7.800e+06	2.400	4471.00
$\text{C}_4\text{H}_9\text{COOH} + \text{H} \rightleftharpoons \text{C}_4\text{H}_9\text{CO}_2 + \text{H}_2$	1.500e+07	1.600	3038.00
$\text{C}_4\text{H}_9\text{COOH} + \text{O} \rightleftharpoons \text{BuCOOH} - 5 + \text{OH}$	9.650e+04	2.680	3716.00
$\text{C}_4\text{H}_9\text{COOH} + \text{O} \rightleftharpoons \text{BuCOOH} - 4 + \text{OH}$	1.908e+05	2.710	2106.00
$\text{C}_4\text{H}_9\text{COOH} + \text{O} \rightleftharpoons \text{BuCOOH} - 3 + \text{OH}$	1.431e+05	2.710	2106.00
$\text{C}_4\text{H}_9\text{COOH} + \text{O} \rightleftharpoons \text{BuCOOH} - 2 + \text{OH}$	1.431e+05	2.710	2106.00
$\text{C}_4\text{H}_9\text{COOH} + \text{O} \rightleftharpoons \text{C}_4\text{H}_9\text{CO}_2 + \text{OH}$	1.460e-03	4.730	1727.00
$\text{C}_4\text{H}_9\text{COOH} + \text{OH} \rightleftharpoons \text{BuCOOH} - 5 + \text{H}_2\text{O}$	5.250e+09	0.970	1590.00
$\text{C}_4\text{H}_9\text{COOH} + \text{OH} \rightleftharpoons \text{BuCOOH} - 4 + \text{H}_2\text{O}$	1.872e+08	1.610	-35.00
$\text{C}_4\text{H}_9\text{COOH} + \text{OH} \rightleftharpoons \text{BuCOOH} - 3 + \text{H}_2\text{O}$	1.404e+08	1.610	-35.00
$\text{C}_4\text{H}_9\text{COOH} + \text{OH} \rightleftharpoons \text{BuCOOH} - 2 + \text{H}_2\text{O}$	1.404e+08	1.610	-35.00
$\text{C}_4\text{H}_9\text{COOH} + \text{OH} \rightleftharpoons \text{C}_4\text{H}_9\text{CO}_2 + \text{H}_2\text{O}$	2.810e+02	2.970	-580.00
$\text{C}_4\text{H}_9\text{COOH} + \text{CH}_3 \rightleftharpoons \text{BuCOOH} - 5 + \text{CH}_4$	4.520e-01	3.650	7154.00
$\text{C}_4\text{H}_9\text{COOH} + \text{CH}_3 \rightleftharpoons \text{BuCOOH} - 4 + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{C}_4\text{H}_9\text{COOH} + \text{CH}_3 \rightleftharpoons \text{BuCOOH} - 3 + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{C}_4\text{H}_9\text{COOH} + \text{CH}_3 \rightleftharpoons \text{BuCOOH} - 2 + \text{CH}_4$	2.705e+04	2.260	7287.00
$\text{C}_4\text{H}_9\text{COOH} + \text{CH}_3 \rightleftharpoons \text{C}_4\text{H}_9\text{CO}_2 + \text{CH}_4$	2.035e+00	3.570	7722.00
$\text{C}_4\text{H}_9\text{COOH} + \text{HO}_2 \rightleftharpoons \text{BuCOOH} - 5 + \text{H}_2\text{O}_2$	8.400e+12	0.000	20440.00
$\text{C}_4\text{H}_9\text{COOH} + \text{HO}_2 \rightleftharpoons \text{BuCOOH} - 4 + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00
$\text{C}_4\text{H}_9\text{COOH} + \text{HO}_2 \rightleftharpoons \text{BuCOOH} - 3 + \text{H}_2\text{O}_2$	5.600e+12	0.000	17690.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$C_4H_9COOH + HO_2 \Rightarrow BuCOOH - 2 + H_2O_2$	5.600e+12	0.000	17690.00
$C_4H_9COOH + HO_2 \rightleftharpoons C_4H_9CO_2 + H_2O_2$	2.500e+12	0.000	24000.00
$C_4H_9COOH + CH_3O_2 \rightleftharpoons BuCOOH - 5 + CH_3O_2H$	8.400e+12	0.000	20440.00
$C_4H_9COOH + CH_3O_2 \rightleftharpoons BuCOOH - 4 + CH_3O_2H$	5.600e+12	0.000	17690.00
$C_4H_9COOH + CH_3O_2 \rightleftharpoons BuCOOH - 3 + CH_3O_2H$	5.600e+12	0.000	17690.00
$C_4H_9COOH + CH_3O_2 \rightleftharpoons BuCOOH - 2 + CH_3O_2H$	5.600e+12	0.000	17690.00
$C_4H_9COOH + CH_3O \rightleftharpoons BuCOOH - 5 + CH_3OH$	1.581e+11	0.000	7000.00
$C_4H_9COOH + CH_3O \rightleftharpoons BuCOOH - 4 + CH_3OH$	1.095e+11	0.000	5000.00
$C_4H_9COOH + CH_3O \rightleftharpoons BuCOOH - 3 + CH_3OH$	1.095e+11	0.000	5000.00
$C_4H_9COOH + CH_3O \rightleftharpoons BuCOOH - 2 + CH_3OH$	1.095e+11	0.000	5000.00
$BuCOOH - 5 \rightleftharpoons C_2H_4 + CH_2CH_2COOH$	2.000e+13	0.000	28700.00
$BuCOOH - 4 + M \rightleftharpoons C_3H_6 + CH_2COOH + M$	1.125e+14	0.500	26591.00
$BuCOOH - 3 \rightleftharpoons C_4H_8 - 1 + HOCO$	3.030e+13	0.270	34667.00
$BuCOOH - 3 \Rightarrow C_3H_5COOH + CH_3$	2.000e+13	0.000	31000.00
$BuCOOH - 2 \rightleftharpoons C_4H_8CO + OH$	3.046e+21	-1.610	57300.00
$BuCOOH - 2 \rightleftharpoons C_2H_5 + C_2H_3COOH$	2.000e+13	0.000	32700.00
$BuCOOH - 2 \rightleftharpoons CO_2 + PC_4H_9$	1.700e+09	1.000	38640.00
$C_4H_9CO_2 + M \rightleftharpoons PC_4H_9 + CO_2 + M$	4.400e+15	0.000	10500.00
$NC_4H_9CO + M \rightleftharpoons PC_4H_9 + CO + M$	1.834e+15	-0.730	12910.00
$BuCOOH - 5 \rightleftharpoons C_4H_7COOH + H$	3.000e+13	0.000	38000.00
$BuCOOH - 4 \rightleftharpoons C_4H_7COOH + H$	3.000e+13	0.000	38000.00
$BuCOOH - 3 \rightleftharpoons C_4H_7COOH + H$	3.200e+13	0.000	34800.00
$BuCOOH - 2 \rightleftharpoons C_4H_7COOH + H$	3.000e+13	0.000	51500.00
$C_4H_7COOH + OH \Rightarrow CH_3CHO + CH_2CH_2COOH$	1.370e+12	0.000	-1040.00
$C_4H_7COOH + OH \Rightarrow C_2H_5CHO + CH_2COOH$	1.370e+12	0.000	-1040.00
$C_4H_7COOH + H \Rightarrow H_2 + CO_2 + C_4H_7 - 1$	4.200e+06	2.100	6900.00
$C_4H_7COOH + OH \Rightarrow H_2O + CO_2 + C_4H_7 - 1$	5.400e+04	2.000	-340.00
$C_4H_7COOH + HO_2 \Rightarrow H_2O_2 + CO_2 + C_4H_7 - 1$	1.000e+11	0.000	11500.00
$C_4H_7COOH + CH_3 \Rightarrow CH_4 + CO_2 + C_4H_7 - 1$	1.400e+01	3.100	9940.00
$C_4H_7COOH + C_2H_5 \Rightarrow C_2H_6 + CO_2 + C_4H_7 - 1$	1.400e+01	3.100	8940.00

Reaction	A (cm-mol-sec-K)	n	E (cal/mol)
$\text{EPE}_4\text{d} + \text{OH} \Rightarrow \text{CH}_3\text{CHO} + \text{EP}_3\text{j}$	1.370e+12	0.000	-1040.00
$\text{EPE}_3\text{d} + \text{OH} \Rightarrow \text{CH}_3\text{CHO} + \text{EP}_3\text{j}$	1.370e+12	0.000	-1040.00
$\text{EPE}_3\text{d} + \text{OH} \Rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{EA}_2\text{j}$	1.370e+12	0.000	-1040.00
$\text{EPE}_2\text{d} + \text{OH} \Rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{EA}_2\text{j}$	1.370e+12	0.000	-1040.00
$\text{EPEEd} + \text{OH} \Rightarrow \text{CH}_3\text{CHO} + \text{C}_4\text{H}_9\text{CO}_2$	1.370e+12	0.000	-1040.00
$\text{EPE}_4\text{d} \rightleftharpoons \text{C}_4\text{H}_7\text{COOH} + \text{C}_2\text{H}_4$	2.000e+12	0.000	47290.00
$\text{EPE}_3\text{d} \rightleftharpoons \text{C}_4\text{H}_7\text{COOH} + \text{C}_2\text{H}_4$	2.000e+12	0.000	47290.00
$\text{EPE}_2\text{d} \rightleftharpoons \text{C}_4\text{H}_7\text{COOH} + \text{C}_2\text{H}_4$	2.000e+12	0.000	47290.00

Appendix C

Procédures d'utilisation du banc d'essai et analyses de risques

C.1 Préambule

Le brûleur à basse pression permet d'analyser des flammes plates prémélangées, en mesurant les profils de fraction molaire des espèces présentes dans ces flammes.

Les gaz frais (combustible, comburant et diluant) arrivent prémélangés dans la chambre de combustion à travers le brûleur. Une étincelle permet l'inflammation des gaz pour former une flamme plate qui se stabilise sur le brûleur à basse pression. Le brûleur étant mobile, la distance vis-à-vis du cône d'échantillonnage peut être adaptée et le prélèvement peut s'effectuer des gaz frais aux gaz brûlés en passant par le front de la flamme.

L'échantillon de gaz prélevé est ensuite chauffé à 200°C derrière le cône par un cordon chauffant afin d'éviter sa condensation jusqu'à l'entrée de la chromatographie en phase gazeuse. Cette dernière analyse le mélange de gaz ainsi prélevé, au moyen de deux détecteurs (FID et TCD), sur base de leur affinité avec la colonne utilisée lors de l'expérimentation.

Le résultat (le temps de rétention) est obtenu à l'aide d'un logiciel "EZChrom®" qui permet de visualiser les différents pics des espèces présentes dans l'échantillon de gaz à l'ordinateur.

C.2 Procédures

C.2.1 Procédure de démarrage

L'opérateur doit avoir des gants en latex et des lunettes de protection lors du remplissage de la triacétine ou de l'éthyl valérate. Cependant, lors de la suite des essais seules les lunettes de protection peuvent être portées.

En cas de problème durant la procédure d'allumage ou les essais, utilisez les boutons d'arrêt d'urgence. Ensuite, reférez-vous à la section "Arrêt d'urgence et procédure de redémarrage"

Avant toute manipulation, l'équipe technique doit être prévenue du démarrage du banc.

1. Vérifier qu'aucun appareil non autorisé se trouve dans les zones ATEX définies dans "Analyse de risques".
2. Brancher l'extracteur ("Extracteur" de gaz représenté à la Figure C.1).



Figure C.1: Extracteur de gaz.

3. Ouvrir le circuit de refroidissement du banc d'essai (VA401Wc puis VA405Wc à la Figure C.2). Vérifier de manière visuelle l'écoulement de l'eau. Si cela n'est pas possible, vérifier que le pressiostat indique bien 2 bar. Cette étape est impérative car, elle permet la commande de l'ouverture des vannes de sécurité.
4. Vérifier que les 3 vannes d'arrivées des gaz sont bien fermées ; la mise à l'air (VA302G) et les 2 vannes noires (VA301G et VA304G)[Figure C.3].
5. Vérifier que la vanne à l'entrée du cordon chauffant 1 est fermée (VA209G, Figure C.4).
6. Mettre en marche le circuit d'eau du brûleur (Vérifier qu'il y a de l'eau dedans et appuyer sur le bouton ON/Ein)[Figure C.5]. Vérifier de façon



Figure C.2: VA401Wc et VA405Wc.

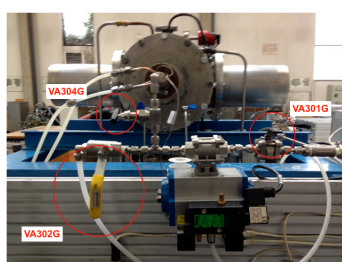


Figure C.3: VA302G, VA301G et VA304G.



Figure C.4: Vanne entrée cordon 1.

visuelle, si le bac contient de l'eau et régler la température du bain à la température souhaitée pour les essais. "La température du bain ne doit pas dépasser 100°C ; de préférence utiliser 90°C comme température maximale".

7. Vérifier que la vanne manuelle de connexion vers la chromatographie est fermée; la vanne verte (VA313G)[Figure C.12].
8. Vérifier que la vanne d'accès à la pompe primaire est bien fermée (VA311G $\rightarrow$ PP320G) [Figure C.7].
9. Vérifier que la vanne d'arrivée d'argon au système d'évaporation est bien

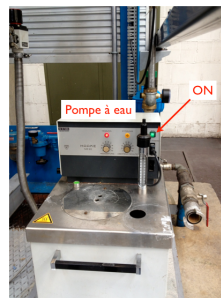


Figure C.5: Pompe à bain thermostatisé : $T = 90^{\circ}\text{C}$ (température maximale).



Figure C.6: VA313G.



Figure C.7: VA311G.

fermée [Figure C.8].

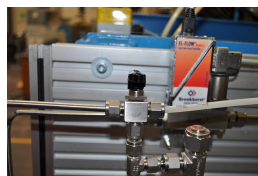


Figure C.8: Vanne manuelle du réservoir.

10. Vérifier que la vanne verte de purge d'éthyl valérate au niveau du système

d'évaporation est bien fermée [Figure C.9].



Figure C.9: Vanne verte purge CEM.

11. Appuyer sur le bouton ON de l'armoire électrique pour mettre en service le banc et allumer les 3 appareils de lecture (**attendre 1 minute**) ainsi que le programme PC [Figure C.10].

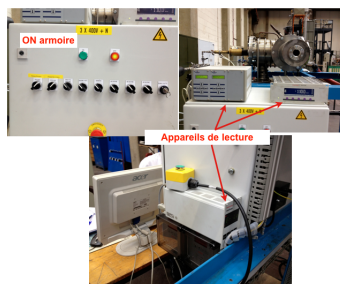


Figure C.10: Bouton ON et appareils de lecture.

Vous pouvez lire à présent les informations de pression et température dans le LabView au niveau du brûleur.

A présent, vous êtes prêts à démarrer le banc d'essai. Celui-ci peut être géré soit de manière **manuelle** soit de manière **automatique** dans l'application LabView.

Dès lors, suivez une des deux instructions.

12. Pour passer en mode manuelle ou automatique, tournez le bouton de l'armoire électrique dans le sens approprié. Pour la suite, lisez en caractère coloré bleu les instructions en mode automatique et en normalisé pour le manuel. Pour certaines opérations, il n'est pas possible de les réaliser autrement que manuellement.

13. Régler dans le LabView la température de l'évaporateur à 180°C (la température maximale est de 200°C).
14. Allumer les cordons chauffant au moyen du bouton sur l'armoire en le tournant vers la droite. La température sera celle dernièrement enregistrée, normalement $T_{cons} = 250^{\circ}\text{C}$. **Allumer les cordons chauffant en cliquant sur le bouton correspondant dans le LabView**
La température affichée dans le LabView est présente à titre d'information, c'est à dire que l'opérateur doit lui-même entrer la valeur lue sur l'appareil.

Si une modification des températures de consigne est nécessaire, enlevez les caches (Figure C.11) et changer la valeur manuellement : appuyer sur la touche S, puis $\uparrow \downarrow$ et enfin rappuyer sur S).

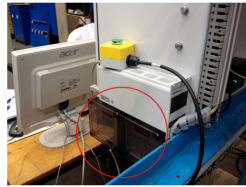


Figure C.11: Position des terminaux des cordons chauffant et du bouton d'allumage.

15. Démarrer les 2 pompes (PP320G et PP318G) en tournant les boutons correspondant sur l'armoire vers la droite. **Démarrer les 2 pompes (PP320G et PP318G) en cliquant sur les boutons correspondant dans le LabView**
16. Ouvrir la vanne de sécurité des pompes (VA319G et VA317G) en tournant le bouton correspondant vers la droite. **Ouvrir la vanne de sécurité des pompes (VA319G et VA317G) en cliquant sur le bouton correspondant dans le LabView.**
17. Faire le vide dans la chambre. Ouvrir dans un premier temps la vanne verte VA313G (Attention, cette vanne n'a pas de butées) (voir Figure C.12). Ensuite, Ouvrir progressivement la vanne manuelle noire de la pompe primaire (voir Figure C.13). Attendez que la pression se stabilise au niveau de 1 mbar . Si la pression ne se stabilise pas, il y a une possibilité de fuite dans le système. Alerter l'équipe technique.



Figure C.12: Vanne manuelle verte pompe secondaire.



Figure C.13: Vanne manuelle pompe primaire.

A ce stade, il est **obligatoire** de tester la vanne de sécurité du brûleur (voir point suivant). En effet, cette vanne coupe l'arrivée des gaz frais dans le brûleur si la pression à l'intérieur de celui-ci dépasse 110 *mbar*.

- (a) La vanne d'arrivée d'air comprimé située au niveau du sol à l'arrière de la chromatographie doit **toujours** rester ouverte avant et après les essais. Pour la chromatographie et la vanne de sécurité, la pression est réglée à 7 *bar* (la pression maximale de l'air comprimé étant de 8 *bar* au niveau du circuit d'alimentation) [Figure C.14].



Figure C.14: Vanne d'arrivée d'air comprimé.

- (b) Mettre en service la vanne de sécurité en tournant le bouton adéquat sur le tableau de commande vers la droite. Celle-ci est couplée avec une autre vanne de sécurité, la VA117Wc, qui coupe l'arrivée de gaz

au niveau des débitmètres en sortie de bonbonne. **Cliquer sur le bouton correspondant dans le LabView afin de mettre en service la vanne de sécurité.**

- (c) Afin d'augmenter la pression dans la chambre, ouvrir la vanne de mise à l'air VA302G (voir Figure C.3) et ouvrir progressivement la vanne à l'entrée du brûleur (VA304G, voir Figure C.3). La pression doit monter (si ces opérations ne font pas grimper la pression suffisamment, ouvrez légèrement la vanne à pointeau VA310G [Figure C.20]). Lorsque la pression dépasse 110 *mbar*, la vanne de sécurité doit s'enclencher (La vanne indique Close). Si elle ne s'enclenche pas informer immédiatement l'équipe technique.

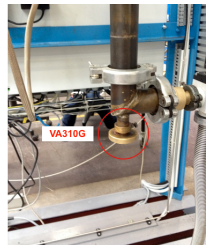


Figure C.15: Vanne réglant la pression dans la chambre de combustion.

- Refermer la vanne de mise à l'air à l'entrée du brûleur (VA302G, voir Figure C.3). Lors de cette opération, la pression descend dans la chambre donc la vanne de sécurité doit se désenclencher pour se remettre en position "Open".
- (d) Vérifier que la vanne VA211Ld en sortie de réservoir d'éthyl valérate soit fermée [Figure C.16].



Figure C.16: Vanne sortie réservoir.

- (e) Faire le vide dans le banc complet (ouvrir les deux vannes manuelles noires après le CEM et avant la vanne de sécurité d'amenée de gaz à la chambre de combustion).
- 18. Brancher la prise d'alimentation au secteur de deux cordons chauffants placés au niveau du système d'injection et régler la température entre 120 et 130°C (régler le bleu à 40 et le rouge à 80).
- 19. Lire la température affichée à l'aide d'un lecteur situé sur le GC. Ce lecteur permet d'afficher la température du cordon du système d'injection (entre le tuyau d'amenée de gaz et le cordon) et la température du gaz à l'intérieur du tuyau. **Cette température sert à vérifier si la compression est isotherme.**
- 20. La pression avant et après compression est affichée dans le labview et provient du capteur de pression située au même niveau que le thermocouple de température de gaz issu de la combustion [FigureC.17].



Figure C.17: Thermocouple-capteur de pression.

C.2.2 Procédure de remplissage du liquide

- (a) Mettre les lunettes de protection ainsi que les gants.
- (b) Mettre la vanne d'arrivée d'argon en position "OFF" [Figure C.8].
- (c) Ouvrir le bouchon du dessus du réservoir à l'aide d'une clé adaptée.
- (d) Remplir à l'aide d'une seringue le réservoir avec le liquide voulu.
- (e) Vérifier à l'aide du tuyau clair en plastique le niveau du remplissage.
- (f) Fermer le bouchon du réservoir.
- (g) Si le banc complet est déjà sous vide, se servir des vannes noire et jaune pour faire le vide aussi dans le réservoir afin d'éviter la présence de l'air dans le système.

- Tourner la vanne noire du réservoir du côté de la vanne manuelle jaune de mise à l'air du banc, comme le montre la Figure C.18.



Figure C.18: Position vanne vide réservoir.

- Ouvrir progressivement la vanne jaune pour faire le vide dans le réservoir du liquide.
- Observer de façon visuelle que le liquide n'entre pas dans la tuyauterie du banc.
- Fermer la vanne jaune puis mettre la vanne noire du réservoir en position perpendiculaire "position *OFF*".

C.2.3 Procédure d'allumage d'une flamme

Après avoir vérifié la vanne de sécurité ainsi que l'étanchéité du système (cfr procédures de démarrage au point 16), passons à l'étape de l'allumage de la flamme.

- Vérifier que la pression dans la chambre soit inférieure ou égale à 1 *mbar*.
- Vérifier que la distance de la tête du brûleur est à 60 *mm* [Figure C.19].

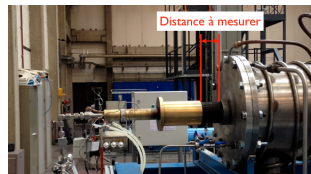


Figure C.19: Tête mobile du brûleur.

- Toujours s'assurer de ne pas dépasser la pression de 100 *mbar* dans la chambre. Si ce n'est pas le cas, desserrer légèrement la vanne à pointeau VA310G [Figure C.20].

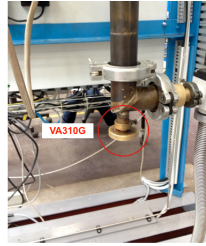


Figure C.20: Vanne à pointeau.

- (d) Introduire l'allumeur dans la chambre de combustion (Figure C.21).



Figure C.21: Position basse de l'allumeur.

- (e) Placer le brûleur à une distance située à 60 mm de la pointe de l'allumeur.
- (f) Vérifier dans le LabView la température de l'évaporateur si elle est à 180°C .
- (g) Ouvrir les bonbonnes de gaz (dans cet ordre : $Ar - O_2 - C_2H_4$) et régler les débits de chaque composant en imposant une pression de 4 bar pour l'Argon et 3 bar pour les autres au niveau des détendeurs des bonbonnes.
- (h) Ouvrir les vannes jaunes situées en dessous des débitmètres (VA104G, VA108G, VA112Wc, VA116Wc voir Figure C.22).
- (i) Dans le LabView, entrer les débits souhaités des différents gaz en $[l/min]$.

$$Ar = 2,4$$

$$O_2 = 2,6$$

$$C_2H_4 = 2,0.$$

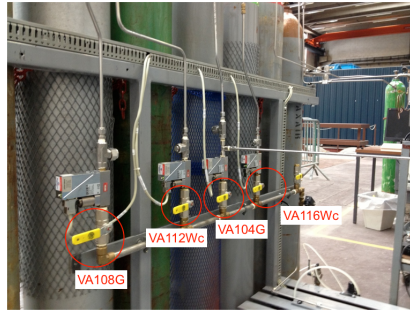


Figure C.22: Position des vannes VA104G, VA108G, VA112Wc, VA116Wc.

NB : Pour l'argon, il est conseillé de régler ce débit au niveau du débitmètre du système d'évaporation, tout en s'assurant que la vanne manuelle noire située après le CEM est bel et bien ouverte. Le débit au niveau du coriflow dépend du débit d'argon. C'est à dire si le débit d'argon est nul, le coriflow ne recevra pas de consigne de débit (mesure de sécurité afin d'éviter de faire passer le liquide seul au niveau de l'évaporateur).

- (j) Vérifier que la pression dans la chambre soit comprise entre 60 et 70 *mbar* si non, l'adapter avec la vanne à pointeau VA310G [Figure C.20].
- (k) Appuyer sur le bouton ON de l'allumeur [Figure C.11]. Ne pas se mettre en face du hublot lors de l'allumage de la flamme.
- (l) Descendre l'allumeur et le verrouiller en position basse à l'aide la bague dorée. **La température pendant la procédure d'allumage de la flamme ne doit pas dépasser 250°C. Vérifier sur le LabView impérativement!.**
- (m) Régler la pression dans la chambre de combustion entre 55 et 65 *mbar* à l'aide de la vanne à pointeau.
- (n) Cliquer sur "START Enregistrement" dans le labview pour démarrer l'enregistrement.
- (o) Mettre la vanne manuelle d'arrivée d'argon au réservoir de l'éthyl valérate et/ou de triacétine en position "ON" (Figure C.23).
- (p) Ouvrir la vanne d'arrivée d'éthyl valérate (VA211Ld, Figure C.16) et régler le débit dans le LabView.



Figure C.23: Position de la vanne d'arrivée d'argon.

- (q) Une fois la flamme stabilisée avec l'ajout de triacétine ou d'éthyl valérate et le débit de Ar réglé, diminuer au fur et à mesure les débits de l' O_2 et du C_2H_4 .

Cette étape se fait en jouant sur la pression de la chambre qui ne doit pas être inférieure à 50 *mbar* jusqu'à ce qu'on atteigne la composition de la flamme voulue.

NB : le débit maximal d'argon équivaut à 2 litres normaux par minute pour l'azote sur l'évaporateur. A titre d'information pour une flamme riche d'éthyl valérate de 7,36 l_N/min (en $[gr/heure]$ pour le liquide et $[l_N/min]$ pour les gaz:

$$\begin{aligned} C_7H_{14}O_2 &= 100 \\ O_2 &= 2.10 \\ Ar &= 5.00 \end{aligned}$$

Pour l'argon, on a 3 l_N/min au niveau du CEM et 2 l_N/min au niveau du débitmètre d'argon de bonbonne.

- (r) Vérifier que la pression dans la chambre est comprise entre 50 et 60 *mbar*. Régler avec la vanne à pointeau (VA310G [Figure C.20]) si nécessaire.

C.2.4 Allumage de la chromatographie en phase gazeuse

Démarrage de la chromatographie en phase gazeuse

- (a) Démarrer l'ordinateur.
- (b) Ouvrir la bonbonne d'hélium et régler la pression sur le détendeur à 4 *bar*.
- (c) Vérifier si le détendeur d'air comprimé en bas du GC affiche 8 *bar*

ou sinon, régler la pression jusqu'à cette valeur.

- (d) Débrancher le câble d'alimentation des vannes pneumatiques " *Power supply* " ,(Figure C.24). NB : Si le câble n'est pas débranché, lors de



Figure C.24: *Power supply de l'actuator.*

l'allumage du GC, le système de vérin fera le vide automatiquement. Afin d'éviter cette situation, il est conseillé de débrancher comme indiquer ci-haut le câble d'alimentation de l'actuator. **Cette étape est à faire lors du démarrage ainsi que de l'arrêt du GC.**

- (e) Appuyer sur le bouton " *ON* " de l'appareil (ce bouton se situe derrière l'appareil) pour allumer la chromatographie en phase gazeuse.
 - (f) Démarrer " *EZChrom,®* " ; TOGA double clic pour commencer.
 - (g) Lancer la méthode "conditionnement" pour nettoyer les colonnes pendant 2 heures.
21. S'assurer toujours de la température maximale des colonnes utilisées lors de votre analyse.
 22. La température du four peut aller jusqu'à 350°C tandis que du boîtier de vannes à 110°C maximum conseillé. Cependant, vous pouvez travailler à 70°C au niveau du boîtier de vanne (confère AUX1 dans la suite).

Allumage du FID

- (a) Ouvrir les bonbonnes d'H₂ puis d'air et régler les détendeurs à 3 *bar*.
- (b) Se servir du boîtier sur le GC pour effectuer les réglages ci-dessous.
- (c) Appuyer sur "Right detector" pour démarrer le FID et faire les

réglages suivants:

$$Temperature = 330^{\circ}C \quad (C.1)$$

$$H_2 = 70 \quad (C.2)$$

$$Air = 350 \quad (C.3)$$

$$MakeupHe = 10. \quad (C.4)$$

- (d) Appuyer sur "ON", on verra s'afficher "Igniting"; attendre jusqu'à ce que l'appareil affiche "ON". Ceci prouve que le FID est bel et bien allumé.
- (e) Si le FID ne s'allume pas au bout de trois essais, fermer les deux bonbonnes (H_2 et Air) puis ouvrir la bonbonne de H_2 puis de l'air et refaire la procédure d'allumage du FID.

Allumage du TCD

- (a) Ceci est à faire lors de la conception d'une méthode dans le logiciel "Ezchrom®".
- (b) Cliquer sur "Control", puis sur "Instrument Status".
- (c) Régler la pression à 250 kPa (pression constante qui implique le débit).
- (d) Régler la température du boîtier TCD à 180°C.
- (e) Régler la température du filament du TCD à 280°C.
- (f) Cliquer sur "Update" pour mettre à jour la consigne donnée.
- (g) Cliquer sur "Detector", un voyant jaune s'allume pour signaler l'allumage.
- (h) Entrer dans la fenêtre "Instrument status" et faire un "Auto zéro".
A faire chaque jour avant manipulation.

Conception d'une méthode de travail

- (a) Cliquer sur "Instrument Set Up", une fenêtre d'affiche sur l'écran.
- (b) Cliquer sur "TCD Righth" et faire les réglages suivants:
 - Detector Parameters: cocher "ON"; Filament (280°C); Input gain (1 à 64x). **le gain permet d'améliorer le rapport signal/bruit de fond. Si le TCD sature, utilisez les valeurs basses au niveau du gain.**

- Acquisition Channel: cocher "ON"; Sampling Rate (50 Hz); Run Time (même que FID); Acquisition Delay (0,00 min); Test Pattern (cocher sur "None").
- (c) Cliquer sur "Oven" pour construire la méthode avec les rampes de température voulues.
- (d) Cliquer sur "Right Inlet PKD" et régler la température à 180°C (T de la chambre TCD).
- (e) Cliquer sur "Right Carrier": Pressure (250 kPa); Choisir "Constant Pressure".
- (f) Cliquer sur "Right Detector" et faire les réglages suivants:
 - Flame: mettre en position "ON".
 - Température: 330°C.
 - Threshold (picoAmpère: pA): 1,0.
 - Flame out Retry: cocher la case.
 - Flow:

$$H_2 = 70 \quad (C.5)$$

$$Air = 350 \quad (C.6)$$

$$MakeupHe = 25. \quad (C.7)$$

- i. Cliquer sur "Aux Zones" et régler "AUX1 = 110°C (température chambre des Vannes) et AUX2 = 320°C (température Méthaniseur)".
- ii. Cliquer sur "Run Table" et gérer les ouvertures et fermetures des vannes (confère schéma GC).
- iii. Cliquer sur "Trigger" et sélectionner "External".
- iv. Enregistrer la méthode ainsi conçue et appuyer sur "Send" pour l'envoyer au GC dans l'onglet "Oven".
- v. Si la méthode a été conçue sur le GC via son clavier, appuyer sur "Get" pour l'afficher sur l'écran du PC.
- vi. Pour lancer la séquence, faire les réglages suivants:
 - Cliquer sur "Sequence".
 - Cliquer sur "Edit Sequence", un tableau s'affiche sur votre écran et le compléter en incrémentant le "File Name".

- Enregistrer la séquence ainsi conçue et cliquer sur "*Run Sequence*", une fenêtre apparaît à l'écran et faire correspondre le numéro de la ligne de la séquence et appuyer sur "*Start*" pour envoyer la séquence au GC.
- (g) Lorsque l'appareil passe en mode stand by; Appuyer sur "*Preprun*", le voyant passe en mode "*Ready to inject*",
- (h) Faire l'injection de l'échantillon et Appuyer sur Start pour lancer l'analyse. Ou encore, Attendre que le GC se mette en position "*Ready to Inject*" pour faire l'injection et appuyer directement sur "*START*" au GC.
- (i) A la fin de la méthode, l'appareil se met en mode "*Stand by*".

Conception d'une séquence d'ouverture de vannes

Le GC a deux modes d'injection d'échantillons : "*Mode automatique à travers le système d'injection*" et "*Mode manuel à l'aide d'une seringue*".

Mode automatique

- (a) Placer la vanne manuelle noire située à l'entrée en position indiquée sur la Figure C.25.



Figure C.25: Vanne entrée GC.

- (b) les vannes 5 fonctionnent en opposition, c'est à dire si la vanne verte est "*ON*", la vanne grise est "*OFF*".
- (c) La vanne 6 sert à commander l'ouverture et la fermeture du vérin.
- (d) La vanne 7 sert envoyer l'échantillon vers la boucle d'échantillonnage du GC.
- (e) La vanne 8 sert à faire le vide au niveau du système d'injection.
- NB : au niveau du logiciel Ezchrom ces vannes correspondent aux "*External Event 5, 6, 7 et 8*" [Figure C.26].

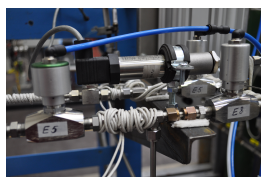


Figure C.26: Vannes automatiques système d'injection.

- (f) La vanne 2 sert à ouvrir la boucle d'échantillonnage pour envoyer l'admission de l'échantillon dans la colonne.
- (g) La vanne 3 sert à isoler la première colonne, dans ce cas la CP-SIL5CB.
- (h) la vanne 4 sert à isoler la deuxième colonne (il s'agit de deux colonnes mises en série dont la Molsieve pour les gaz permanents et la RTX1 qui sert de restriction de débit pour le microTCD). NB : dans le logiciel Ezchrom, ces vannes correspondent aux "External Event 2, 3 et 4".

Voici un exemple d'une méthode de commande de ces vannes:

- 0.01 E_8 ON (faire le vide dans le système d'injection sauf dans le vérin).
- 0.04 E_8 OFF.
- 0.05 E_6 ON (faire le vide dans tout le système d'injection).
- 0.06 E_5 ON (ouverture de la vanne pour l'arrivée de l'échantillon dans le vérin).
- 1.30 E_5 OFF.
- 1.32 E_6 OFF (compression de l'échantillon).
- 1.37 E_7 ON (ouverture de la vanne pour amenée l'échantillon dans la boucle).
- 1.39 E_2 ON (ouverture de la vanne pour injecter l'échantillon dans la colonne).
- 1.49 E_2 OFF (fermeture de la vanne au niveau de la boucle).
- 1.50 E_7 OFF.
- 1.60 E_8 ON (idem que 0.01).
- 1.64 E_8 OFF.
- 3.71 E_4 ON (ouverture vanne pour isoler la colonne 2).

- 36.00 E_4 OFF (fermeture vanne pour éluer de deux colonnes).

La première colonne est le temps, la deuxième les vannes et la troisième l'action.

Mode manuel

En mode manuel, l'injection se fait à l'aide d'une seringue.

- (a) Mettre la vanne manuelle noire en position indiquée sur la Figure C.27.



Figure C.27: Injection seringue.

- (b) Seules les vannes 2 ,3 et 4 sont prises en compte dans la méthode d'injection, les autres vannes peuvent être mises en position " OFF".
NB :Voici un exemple de la séquence à mettre dans la méthode.

- 0.01 E_8 OFF.
- 0.04 E_8 OFF.
- 0.05 E_6 OFF.
- 0.06 E_5 OFF.
- 1.30 E_5 OFF.
- 1.32 E_6 OFF.
- 1.37 E_7 OFF.
- 1.39 E_2 ON (ouverture de la vanne pour injecter l'échantillon dans la colonne).
- 1.49 E_2 OFF (fermeture de la vanne au niveau de la boucle).
- 1.50 E_7 OFF.
- 1.60 E_8 OFF (idem que 0.01).
- 1.64 E_8 OFF.
- 3.71 E_4 ON (ouverture vanne pour isoler la colonne 2).
- 36.00 E_4 OFF (fermeture vanne pour éluer de deux colonnes).

C.2.5 Procédure d'arrêt du banc d'essai

L'arrêt du matériel expérimental peut se faire de deux façons différentes, selon les cas. Il peut être normal, c'est-à-dire à la fin des essais ; soit encore urgent, en cas d'un dysfonctionnement observé au cours de l'opération des essais.

Arrêt normal

1. Fermer la vanne manuelle amenant la triacétine ou de l'éthyl valérate (VA211Ld, Figure C.16).
2. Dans LabView, mettre la valeur du débitmètre de la triacétine ou de l'éthyl valérate à 0.
3. Laisser le débit d'argon au niveau du système d'évaporation pendant 10 minutes.
4. Régler la température de l'évaporateur à 30°C dans le LabView.
5. Fermer la vanne manuelle VA301G (voir Figure C.3) pour éteindre la flamme.
6. Ouvrir la vanne manuelle VA301G (voir Figure C.3) pour laisser passer les gaz.
7. Fermer les bonbonnes en suivant l'ordre C_2H_4 , O_2 , et Ar . Dévisser les vannes manuelles sur les détendeurs afin de mettre la pression au niveau des détendeurs à 0.
8. Attendre que la pression sur les détendeurs indique 0.
9. Initialiser les débits dans LabView à 0.
10. Fermer les vannes manuelles jaunes d'arrivée des gaz (VA104G, VA108G, VA112WC et VA116Wc).

Mettre la chromatographie en phase gazeuse en mode stand by à l'aide d'une méthode appropriée.

- (a) Débrancher l'alimentation " *Power supply actuator* " derrière le GC.
- (b) Si la méthode ne permet pas d'éteindre le FID, appuyer sur " *Right Detector* " puis sur " *OFF* " pour le faire.

- (c) Fermer les bonbonnes de H_2 puis de l' Air; si la méthode permet d'éteindre le FID (vérifier sur " *Right Detector*" si Flame est sur la position " *OFF*").
 - (d) Appuyer sur " *OFF*" derrière le GC.
 - (e) Fermer la bonbonne d'hélium.
11. Vérifier si la pression dans la chambre commence à diminuer. Attendre que celle-ci soit inférieure à 1 *mbar*. Si la pression ne diminue pas assez, utilisez la vanne à pointeau.
 12. Fermer la vanne manuelle VA301G et VA304G (Figure C.3).
 13. Fermer la vanne VA303G (bouton disposé sur l'armoire électrique).
 14. Fermer les vannes VA311G et VA312G des pompes (Figure C.7 et Figure C.12) puis arrêter la vanne de sécurité des pompes(VA317G/VA319G) soit manuellement, **soit dans le LabView**.
 15. Éteindre les pompes (vannes PP320G et PP318G)soit manuellement sur l'armoire ou **dans le LabView**.
 16. Eteindre les deux lecteurs de pression sur l'armoire ou encore sur le lab-view selon le mode d'utilisation (manuelle ou automatique).
 17. Éteindre les cordons chauffants (bouton sur l'armoire électrique).
 18. Eteindre les cordons chauffants du système d'injection. **En mode automatique, éteindre les cordons en cliquant sur le bouton correspondant**
 19. Éteindre le circuit d'eau chaude du brûleur. Appuyer sur " *ON/Ein*" .
 20. Laisser circuler l'eau de refroidissement jusqu'à la température, dans la chambre de combustion, de 40°C.
 21. Fermer l'eau : d'abord VA401Wc puis VA405Wc (voir Figure C.2).
 22. Arrêter le LabView en cliquant sur STOP acquisition; puis fermer la fenêtre.
 23. Ne pas éteindre l'ordinateur si le GC est mis en Stand bye.
 24. Fermer l'extracteur de gaz.

25. Appuyer sur "OFF" sur l'armoire électrique. Le GC n'est pas alimenté par le banc.
26. En cas d'arrêt complet du banc pour une longue durée, procéder à la purge du système d'évaporation.
 - (a) Laisser le débit d'argon au niveau du débit-mètre du système d'évaporation.
 - (b) Laisser le CEM à 180°C .
 - (c) Ouvrir la vanne manuelle verte qui sert de purge. (voir Figure C.28).



Figure C.28: *Purge système d'évaporation.*

- (d) Taper 100 dans le labview comme débit au niveau du coriflow; Le débit ne sera plus stable lorsque le gaz passera au niveau de la vanne du débit-mètre; car il sert au liquide (pas de souci à ça).
- (e) Après 5 minutes, retaper 0 puis arrêter tout le système.
- (f) Fermer toutes les vannes manuelles afin d'isoler cette partie de l'installation.

Arrêt d'urgence et procédure de redémarrage

En cas de tout dysfonctionnement se trouvant dans ce présent manuel (pression haute dans la chambre de combustion supérieure 100 *mbar*, haute température dans la chambre au moment de l'allumage de la flamme (T est supérieure à 240°C), fuite de gaz sur n'importe quelle partie du circuit; fuite ou manque d'eau dans le circuit, etc.), il est conseillé d'utiliser le mode arrêt d'urgence. Les boutons d'arrêt sont fixés sur le banc de façon à y être accessible sur n'importe quelle partie où se trouveraient les deux opérateurs.

Après tout arrêt d'urgence, informer les techniciens pour une éventuelle réparation.

La mise en marche de l'outil expérimental, après un arrêt d'urgence, doit se faire, impérativement, en suivant la procédure d'arrêt normal en allumant préalablement l'armoire électrique et suivre le démarrage normal pour vider les gaz dans les conduites.

Entretien du banc

1. Après 6 semaines de test de flammes, prévoyez un arrêt complet du banc " *même si tout marche bien*".
2. Faire le vidange des pompes afin de changer l'huile (tâche à demander à l'équipe technique).
3. Ouvrir l'entrée du brûleur et vérifier l'état des billes à la tête du brûleur.
4. Vérifier les circuits de pompage puis refermer le tout.

C.3 Analyse de risques**C.3.1 Zones ATEX**

Zones ATEX concernant le dispositif:

1. Bonbonnes de gaz : Zone 2 dans une sphère de 50 *cm* autour de la tête des bonbonnes.
2. Concernant les conduites d'aménées des gaz en métal (acier inoxydable), aucune zone ATEX n'est à définir, elles sont réputées étanches. A chaque modification du système, un test d'étanchéité est à effectuer comme le décrit la " *Procédure de démarrage*".
3. Concernant la chambre de combustion, la vanne de sécurité VA303G, permet de garder le mélange de gaz à basse pression dans cette chambre. Le mélange ne se trouve pas dans des conditions explosives à ces basses pressions. Toutefois, si une surpression arrive à l'entrée de cette chambre de combustion (pression supérieure à 110 *mbar*), la vanne de sécurité VA303G se ferme et empêche ainsi un risque d'explosion de la chambre. Avant toute manipulation, la " *Procédure de démarrage* " stipule un test de bon fonctionnement de cette vanne VA303G. Aucune zone ATEX n'est donc à définir pour la chambre de combustion.
4. Concernant l'évacuation des gaz, les gaz brûlés pompés par les pompes primaires PP318G et PP320G sont également à basse pression et ne présentent aucun risque d'explosion ou d'inflammation dans les flexibles en acier inoxydable. Pas de zone ATEX à définir pour cette partie du dispositif.

C.3.2 Risque d'explosion

Comme expliqué dans les définitions de zone ATEX, en fonctionnement, le dispositif expérimental se trouve à basse pression et le risque d'explosion n'est donc pas à considérer.

Cependant, en cas de panne d'un élément du système, des sécurités ont été placées:

1. A l'entrée de la chambre de combustion: une vanne d'arrêt (VA303G) se ferme automatiquement en cas de coupure d'électricité ou de pression supérieure à 110 *mbar* dans la chambre de combustion. Cette vanne empêche donc une pression de gaz trop importante dans la chambre afin d'éviter toute explosion. Selon la "*procédure de démarrage*", cette vanne est initialement testée avant l'injection des gaz pour vérification de son bon fonctionnement.
2. Les débitmètres massiques sont également en arrêt automatique (normalement fermé) lors d'une coupure d'électricité pour éviter une surpression des gaz dans les conduites.
3. Une vanne de sécurité est ajoutée juste après les débitmètres massiques, qui se ferme lors d'une coupure d'électricité (normalement fermée).
4. Les procédures sont explicites sur la vérification des pressions avant, pendant et après les manipulations du système expérimental. Un contrôle permanent des pressions est réalisé lors de l'utilisation de ce brûleur.

C.3.3 Risque de fuite de gaz

Avant toute manipulation et injection des gaz, une vérification d'étanchéité est effectuée par lecture de la basse pression. Si la pression lue n'est pas telle qu'elle est mentionnée dans les procédures, des tests d'étanchéité sont réalisés. En introduisant dans le système expérimental de l'argon ou de l'oxygène afin d'augmenter la pression, il suffit de placer de l'eau savonneuse sur les connexions pour détecter et situer la fuite.

De même, après chaque démontage d'une partie du système, un test de vérification est effectué afin de s'assurer de la bonne étanchéité des raccords comme il est stipulé dans la "*procédure d'allumage d'une flamme*".

C.3.4 Risque de contamination des produits chimiques

En travaillant avec des composés liquides à température ambiante tels que l'éthyl valérate, l'utilisateur doit porter des gants en latex pour éviter toute contamination et des lunettes de sécurité pour se protéger des éventuelles projections.

La "*procédure d'allumage d'une flamme*" le stipule avant toute manipulation.